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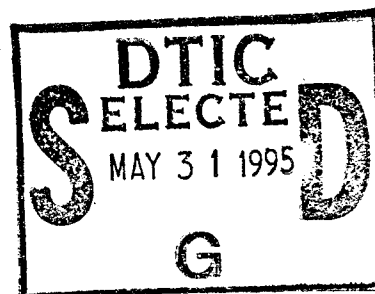
Installation Restoration Research Program

Impacts of Sorption on In Situ Bioremediation of Explosives-Contaminated Soils

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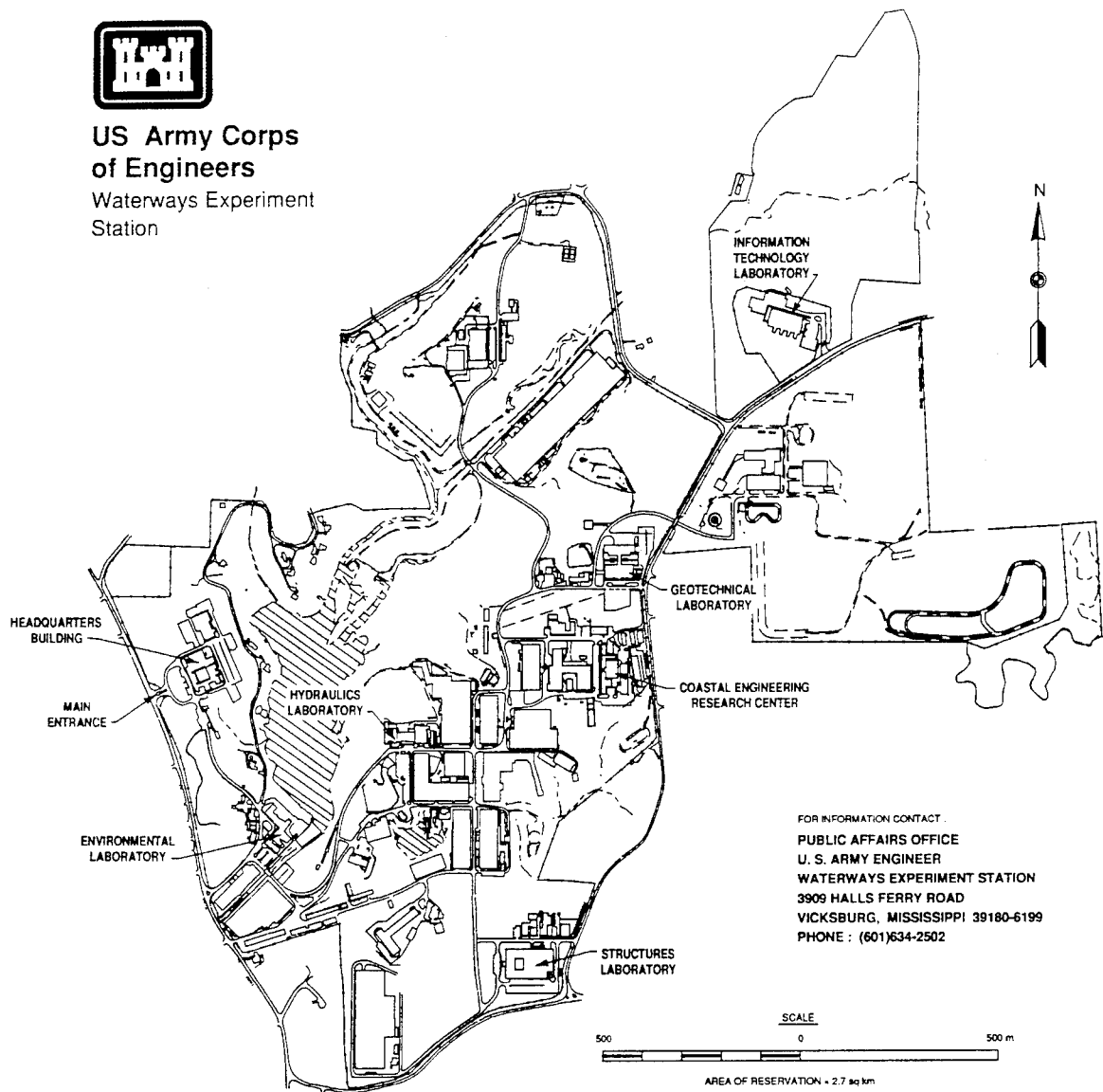
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Preface

This report was prepared by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The research was funded by the Installation Restoration Research Program (IRRP), Work Unit AF25-ET-004. The Program is managed by Dr. John Cullinane, WES; Captain Kevin Keehan was the Technical Monitor for the U.S. Army Environmental Center; and Mr. Richard Waples was the Technical Monitor for U.S. Army Corps of Engineers Military Programs. Personnel who cooperated in the execution of the study and the preparation of this report include Dr. Judith C. Pennington and Dr. William M. Davis of the Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL; Mr. Tommy E. Myers of the Environmental Restoration Branch (ERB) and Ms. Trudy J. Olin, Environmental Applications Branch (EAB), Environmental Engineering Division (EED), EL; Ms. Tiarre A. McDonald and Ms. Charolett A. Hayes of ASci Corporation, McLean, VA; and Mr. Dan M. Townsend, North Carolina State University, Raleigh, NC. The report was reviewed by Drs. James M. Brannon, Douglas Gunnison, and Herbert L. Fredrickson, EPED, and Mr. Daniel E. Averett, EED. Dr. Douglas Gunnison, EPEB, provided the figures of bioremediation scenarios.

The report was prepared under the general supervision of Dr. Richard E. Price, Acting Chief, EPEB; Mr. Craig Fischenich, Acting Chief, EAB; Mr. Donald L. Robey, Chief, EPED; Mr. Norman R. Francingues, Acting Chief, EED; and Dr. John W. Keeley, Director, EL.

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1 Introduction

Adsorption/Desorption Processes and Solution Phase Concentration

Adsorption and desorption processes often exert a dramatic effect upon movement of contaminants through soils (Freeze and Cherry 1979; Thibodeaux 1979; Curtis, Roberts, and Reinhard 1986; Brusseau and Rao 1989; Mercer, Skipp, and Giffin 1990; Travis and Doty 1990). For example, slow desorption rates may limit microbial access to contaminants during in situ bioremediation. Contaminants bound to intraparticle pores and adsorbed to walls of minute tortuous channels must desorb before diffusing into areas where microbial degradation is occurring. On the other hand, highly contaminated soils may contain crystalline explosives (free product) that serve as a continuous source of dissolved contaminant. In this case, solution phases in the soil may remain at saturation, i.e., may contain concentrations at or near the aqueous solubility of the explosive. If solution phase concentrations are sufficiently high to be detrimental to the degrading microflora, bioremediation may be inhibited.

The possibility also exists for *facilitated transport* of explosive. In facilitated transport solution phase concentrations *appear* to exceed aqueous solubility of the contaminant. This occurs because of association of the contaminant with suspended organic material in the solution phase. Effects of facilitated transport upon bioavailability are unknown.

Adsorption and desorption processes of organic contaminants in soils have been widely studied in recent years (Hassett and Anderson 1982; Karickhoff 1981; Karickhoff, Brown, and Scott 1979; Landrum et al. 1984; O'Connor and Connolly 1980; Voice, Rice, and Weber 1983). However, much of the data available has been limited to contaminant-amended soils rather than anthropogenically contaminated soils from the field. Field-contaminated soils have been subjected to fluctuations in environmental factors such as temperature, moisture, leaching, sunlight, penetration by plant roots, and even perturbation by burrowing animals and insects. Contaminant binding in soils subjected to such dynamic changes may differ greatly from binding in amended soils. Time of contact between soil and contaminant also affects sorption characteristics (Grant,

Jenkins, and Golden (in preparation)). Longer exposure times may allow contaminants to migrate into intraparticle sorption sites in clay particles or in organic matter. As clay and organic matter swell and shrink with wetting and drying cycles, adsorption to less accessible areas may increase. Desorption from these pores is much slower than from surface sorption sites (Brusseau and Rao 1989). Therefore, laboratory results obtained by quickly amending soils with contaminants of interest must be verified using field-contaminated soils. Information on desorption of contaminants of interest from field-contaminated soils is extremely limited. Therefore, this study used field-contaminated soils.

Contaminants

Adsorption of 2,4,6-trinitrotoluene (TNT) to soils has been demonstrated to exhibit a rapid initial component and a slower long-term component (Pennington and Patrick 1990). Desorption was also found to be rapid, but a small fraction was recalcitrant. Pennington and Patrick (1990) found that soil adsorption and desorption correlated most highly with cation exchange capacity and clay content of soils, and to a lesser extent with soil organic carbon.

TNT undergoes microbial degradation in soils to several persistent intermediate compounds of greater environmental hazard than the parent compound (Kaplan and Kaplan 1982). Sorption properties and microbial availability of most of these intermediates have not been studied. Therefore, these will be a focus of this study.

The soil partition coefficient for 1,3,5-hexahydro-1,3,5-trinitrohydrazine (RDX) is similar to that of TNT (Sikka et al. 1980). As is true for TNT, clay content is more important than organic carbon content in RDX sorption (Sikka et al. 1980).

Objectives

The objectives of this study were as follows:

- a. To characterize desorption of TNT, TNT transformation products, RDX, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in field-contaminated soils.
- b. To quantify solution phase availability of TNT, RDX, and HMX in highly contaminated soils.
- c. To enhance bioavailability of TNT, RDX, and HMX in soils.

2 Materials and Methods

Collection of Soils

Explosive-contaminated soils were obtained from Department of Defense facilities known to have been exposed to TNT, RDX, and/or HMX. Two soil samples, one from the surface (Crane Sifter) and one from a depth of approximately 45 cm (17.7 in.) (Crane 1.5), were obtained from Crane Naval Weapons Support Center, Crane, IN, in the vicinity of an old sifter and conveyer belt. These soils contained higher concentrations of RDX than TNT or HMX. The two Crane samples are Burnside soils in the Wellston-Berks-Ebal series, which is characterized as deep and moderately deep, gently sloping to very steep, well-drained and moderately well-drained soils formed in loess and material weathered from sandstone, siltstone, and shale on uplands (U.S. Soil Conservation Service 1985). A soil sample highly contaminated with TNT, but relatively low in RDX and HMX, was obtained from the abandoned Weldon Springs Ordnance Works, St. Charles County, MO. The sample was taken from the Weldon Springs Training Area, which has been described as having a gently undulating surface of unconsolidated Quaternary loess and glacial drift deposited on residuum and weathered Keokuk and Burling Limestones of Lower Mississippian age (Schumacher, Lindley, and Anderson (in preparation)). Another soil highly contaminated with TNT (12,800 mg TNT/kg) (894 grains/lb) was obtained from Hastings East Industrial Park, Hastings, NE. The sample, taken from the Flemings Pond Site, was described in the field as clayey, sandy silt, red-brown to silty lean clay, gray-brown to dark brown.

Soils were transported to the laboratory and sieved to 2 mm (0.08 in.) to remove any large clumps. The sieved soils were each thoroughly mixed by spreading the soil in a flat pan and turning repeatedly with a shovel. The soil was then poured repeatedly between two 22.7-L (6-gal) plastic buckets to ensure homogenization. Once well-mixed, the soils were sampled for explosives analysis and other soil characterization tests described below. Soils were stored in air-tight 22.7-L (6-gal) plastic containers at 4 °C until used in the study.

Soil Characterization

Prior to investigation of explosives sorption, homogenized soils were subsampled for analysis of explosives and other soil characteristics. Explosives concentrations in the soils were determined using U.S. Environmental Protection Agency (USEPA) Method SW846-8330 (USEPA 1990). Total organic carbon was determined by American Public Health Association (1989) Method 5310 D. Percent organic matter was determined by the Wakley-Black method as modified by Debolt (Debolt 1974). Soil pH was determined on magnetically stirred soil slurries (1:1, soil: distilled deionized water) using a Beckman Model SS-3 pH meter (Beckman Instruments Inc., Fullerton, CA) (USEPA 1986). Cation exchange capacity (CEC) was determined by the ammonium saturation method (Plumb 1981). Extracts for CEC determinations were analyzed according to USEPA Standard Method 350.1 (USEPA 1982). Conductivity was determined according to the procedure of Rhoades (1982). Particle size distribution was determined by the method of Day (1956) as modified by Patrick (1958). Oxalate extractable iron (Fe), aluminum (Al), manganese (Mn), and calcium (Ca) were determined according to the method of Brannon and Patrick (1985). Metals were assayed on a Beckman Spectra Span IIIB Argon Plasma Emission Spectrophotometer (Applied Research Laboratories, Dearborn, MI). Additional analyses included nitrate nitrogen, total Kjeldahl nitrogen, ammonia nitrogen, and organic nitrogen (USEPA 1990).

Desorption Kinetics

Soils were equilibrated with distilled deionized (DDI) water in 250-mL (8.45-oz.) polycarbonate centrifuge bottles at a soil-to-water ratio of 1:4 (30 g (1.06 oz.) soil to 120 mL (4.056 oz.) DDI water) on a reciprocating shaker at 280 excursions per minute. At appropriate sampling times (0.5, 1, 2, 6, 24, 48, and 120 hr), samples were centrifuged at 5,000 units relative centrifugal force, the solution phase was filtered through a Whatman Type GD/F 4-micron prefilter and a Gelman 1-micron glass fiber filter and analyzed for explosives (USEPA 1990). The kinetics investigation was carried out in triplicate for each soil examined.

Sequential Desorption

Sequential batch leaching of explosives from the contaminated soils was performed by challenging soils with six successive aliquots of DDI water for 24 hr (Myers and Brannon 1988). Equilibrations and subsequent separations of phases were performed as described above for the desorption kinetics investigation. The solution phase of each of the six successive aliquots was analyzed for explosives (USEPA 1990).

Enhanced Desorption

The effect of heat on the desorption of explosives from soils was investigated by repeating the kinetics and sequential desorption procedures described above at 40 and 55 °C with Crane Sifter soil. Temperature was maintained by incubating tests in a rotary shaker water bath. Effects of surfactants on desorption were determined on Crane Sifter soil with 1,2, and 3 percent (w/w) solutions of either Alfonic® 1012-60 ethoxylate (Vista Chemical Company, Austin, TX) or Tween® 80 (ICI Americas Inc., Wilmington, DE) in DDI water. Based on the results of this test and the manufacturer's recommendations, subsequent surfactant tests with other soils were conducted with 3-percent surfactant.

Column Tests

Column tests were conducted on Crane 1.5 soil sieved to 4 mm (0.16 in.). A 15-cm (6-in.) by 4.42-cm (1.74-in.) diameter column in an upflow configuration was used (Figure 1). Contaminated soil was loaded into the column in two lifts, at existing water content, but was not packed. To saturate the soil column, equilibrate the soil-water system, and prime the inlet-outlet piping, de-aired, distilled-deionized water was pumped into the column until water appeared at the outlet port (Figure 2). The pump was stopped and the outlet was sealed. The column was allowed to rest for 2 weeks. After the equilibration period, continuous flow of de-aired, distilled-deionized water was initiated using a constant volume pump. The average pore water velocity was 1.08×10^{-4} cm/sec (0.4×10^{-5} in./sec). This velocity, the approximate velocity expected for a hydraulic gradient of one and a hydraulic conductivity of 10^{-4} cm/sec (4×10^{-4} in./sec), was selected to represent saturated flow in silt. Duration of the leaching test was approximately 35 days.

Effluent was sampled at approximately 40-hr intervals. Samples were analyzed by USEPA Method 8330 (reverse phase HPLC) (USEPA 1990) for TNT, RDX, HMX, and tetryl; TNT transformation products, 2-amino-4,6-dinitrotoluene (2A) and 4-amino-2,6-dinitrotoluene (4A); TNT decomposition products, 1,3,5-trinitrobenzene (TNB), and 1,3-dinitrobenzene (DNB); and 2,4-dinitrotoluene (2,4DNT). Approximately 19 void volumes were eluted.

The leaching experiment was followed by a chloride tracer study to determine the dispersion coefficient for the soil column (Levenspiel 1972). Following the chloride tracer study, the soil column was frozen and sectioned for chemical analysis for the previously described explosive compounds.

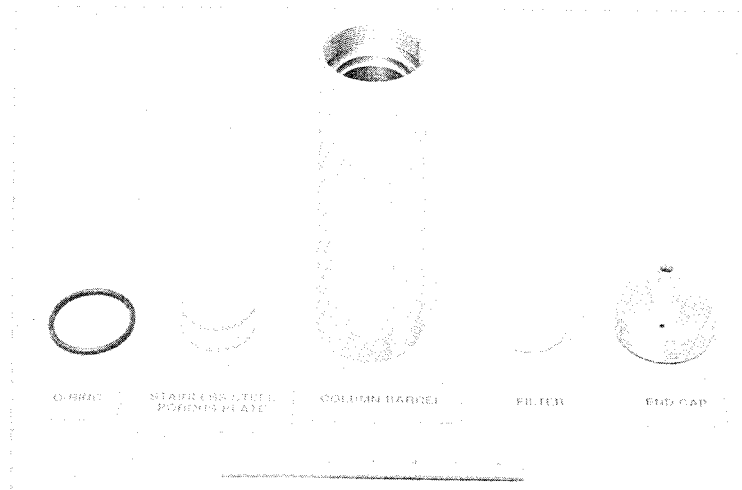


Figure 1. Stainless steel column and components

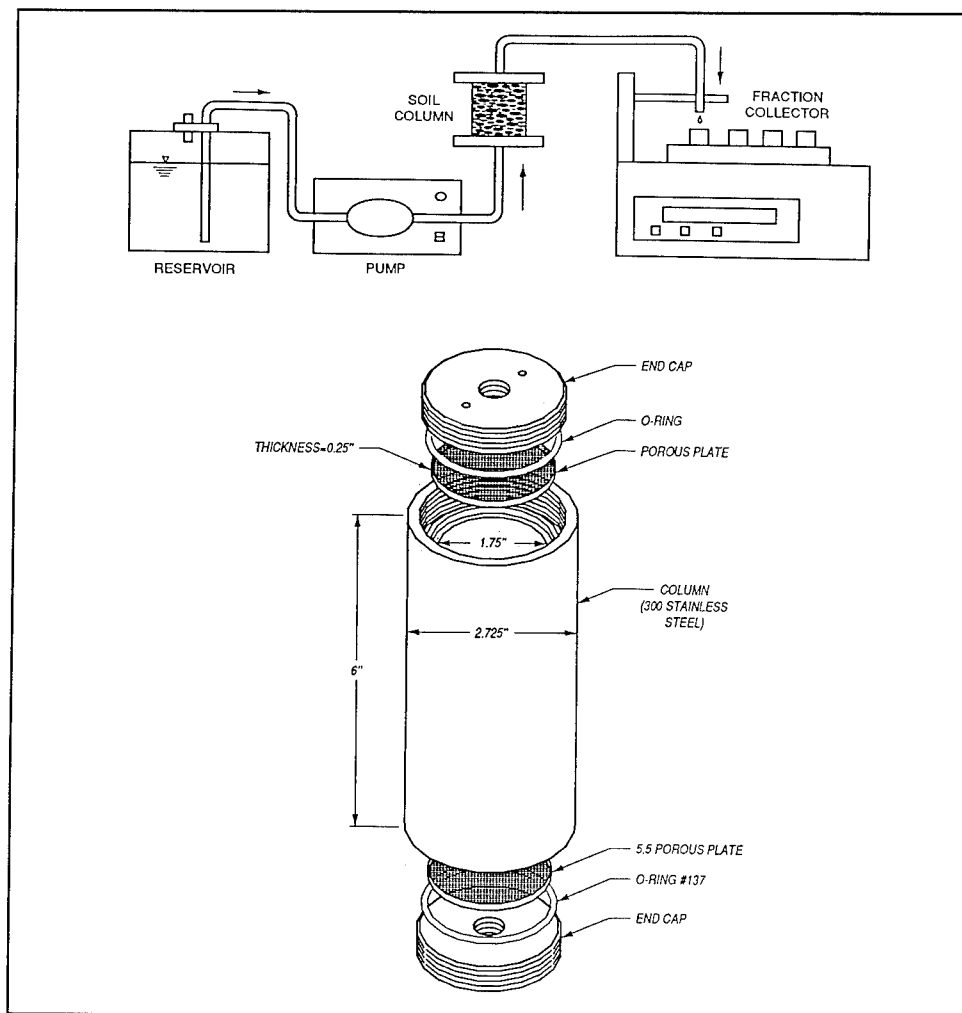


Figure 2. Soil column test apparatus

3 Results and Discussion

Soil Characterization

The concentration of TNT in test soils ranged over several orders of magnitude (Table 1). Only Crane Sifter and Crane 1.5 soils had detectable levels of RDX and HMX, but the two soils differed significantly in concentration of each. Crane Sifter was higher than Crane 1.5 in all three explosives. Crane 1.5, which was taken from a depth of 45 cm, exhibited three orders of magnitude less RDX and HMX and two orders of magnitude less TNT than the surface soil (Crane Sifter) collected at the location. Two of the soils, Crane 1.5 and Hastings, contained detectable levels of the TNT transformation products TNB, 2,4-DNT, 4A, and 2A.

The soils represented a broad range of chemical and physical properties (Table 2). Total organic carbon ranged from a low of 0.745 percent in the Crane 1.5 soil to a high of 3.11 percent in the Weldon Springs soil. All of the soils could be characterized as silt loam to silty clay loam according to particle size distribution. Cation exchange capacities represented a

Table 1
Concentration of Explosives and Related Compounds in Soils (mg/kg)

Soil	TNT	RDX	HMX	2A	4A	2,4DNT	TNB
Weldon Springs Detection Limits	41,800 ¹ 0.25	<1.00 1.00	<2.20 2.20	M	M	0.25 0.25	121 0.25
Hastings Detection Limits ²	12,800 ³ 0.25	<1.00 1.00	<2.20 2.20	30.7 0.25	34.5 0.25	21.1 0.25	32.2 0.25
Crane Sifter Detection Limits ⁴	1,495 0.25	11,200 1.00	1,250 2.20	<25.0 0.25	<25.0 0.25	<25.0 0.25	<25.0 0.25
Crane 1.5 (2mm) Detection Limits	25.8 0.25	52.7 1.00	5.82 2.20	0.634 0.25	0.730 0.25	<25.0 0.25	0.368 0.25
Crane 1.5 (4mm) Detection Limit	9.47 0.931	31.2 0.445	4.80 0.755	NA	NA	<0.744 0.744	0.544 0.352

¹ Sample was diluted 1:250 for this analyte only.

² Instrument detection limits without sample dilution.

³ Sample was diluted 1:100 for this analyte only.

⁴ Sample was diluted 1:100 prior to analysis.

M Any peaks were masked by the predominance of the TNT peak.

NA Analyte not assayed.

Table 2
Chemical and Physical Characteristics of Soils

Soil	Particle Size (%)			pH	%OC	CEC (meq/100g)	Conductivity (dS/m)	TKN (mg/kg)	NO ₃ -N (mg/kg)	NH ₃ -N (mg/kg)	Oxalate Extractable Metals (mg/kg)			
	Sand >50 μ	Silt 2-50 μ	Clay <2 μ								Fe	Al	Mn	Ca
Hastings	18	54	28	6.64	1.37	26	2.021	1,325	18.0	23.8	13,450	12,625	342.5	4,620
Weldon Springs	27	54	19	6.92	3.11	18	2.56	1,494	12.6	30.35	1,437	8,955	1,438	3,698
Crane Sifter	19	58	23	6.66	1.30	15	2.11	1,022.5	342	14.8	17,400	10,900	1,025	2,705
Crane 1.5 (2mm)	34	45	21	7.15	0.745	64	2.021	665.5	13.8	21.3	25,000	15,025	1,118	4,775
CEC - Cation exchange capacity TKN - Total Kjeldahl nitrogen NO ₃ -N - Nitrate nitrogen NH ₃ -N - Ammonia nitrogen											Fe - Iron Al - Aluminum Mn - Manganese Ca - Calcium			
dS/m - deciSiemen per meter %OC - percent organic carbon														

fairly broad range from a low of 15.1 meq/100 g for the Crane Sifter soil to 63.6 meq/100 g for the Crane 1.5 soil.

Desorption Kinetics

Weldon Springs soil

Solution phase concentration increased rapidly during the first 24 hr, and slowly or not at all thereafter (Figure 3). Although concentrations of 4A were only slightly less than concentrations of 2A initially, 4A remained near steady state throughout the 5-day test period. After 5 days, the solution phase concentration of TNT exceeded aqueous solubility (130 mg/L (75.8 grains/gal)) by about 20 percent. Since initial soil concentrations of this compound were high, a saturated or near saturated solution phase after 24 hr most likely reflects solubilization of crystalline explosive from the soil. Continued rise above aqueous solubility may be due to temperature increases caused by friction during prolonged shaking or to compound sorbed to suspended or dissolved material too small to be removed in the filtration step (facilitated transport).

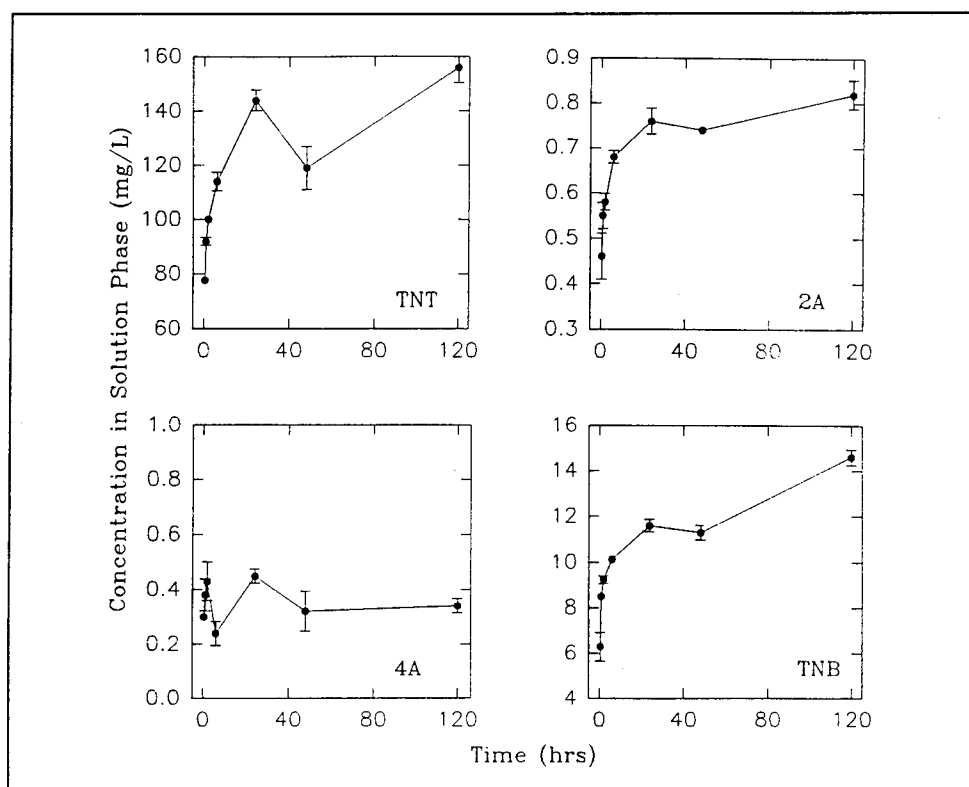


Figure 3. Desorption kinetics for TNT and three of its transformation products (2A, 4A, and TNB) in Weldon Springs soil. Vertical bars are standard errors of the mean of three replicates

Hastings soil

Desorption of TNT, 2A, 4A, and TNB reached steady state (no significant change in solution phase concentration at the P.05 level) after 24 hrs (Figure 4). The 4A was at steady state after 2 hr. The solution phase concentration of TNT at steady state was 132 ± 2.3 mg/L (77 ± 1.3 grains/gal) which is equal to the aqueous solubility. Steady-state concentrations of 2A and 4A were about three times higher than maximum concentrations found in Weldon Springs soil, even though the initial soil concentration of TNT in Weldon Springs soil (41,800 mg/kg) was higher than in Hastings soil (12,800 mg/kg). The steady-state concentration of TNB was about one-seventh the maximum concentration observed in Weldon Springs soil. This suggests that transformation to TNB is more dependent upon soil characteristics than upon the initial TNT concentration. Recent evidence suggests that transformation of TNT to TNB may be mediated by microorganisms or by abiotic chemical processes in soils as well as by light (Gunnison et al. (in preparation)).

Crane Sifter soil

Aqueous kinetics. The desorption kinetics curves for TNT and 4A were similar to those obtained with Hastings and Weldon Springs soil.

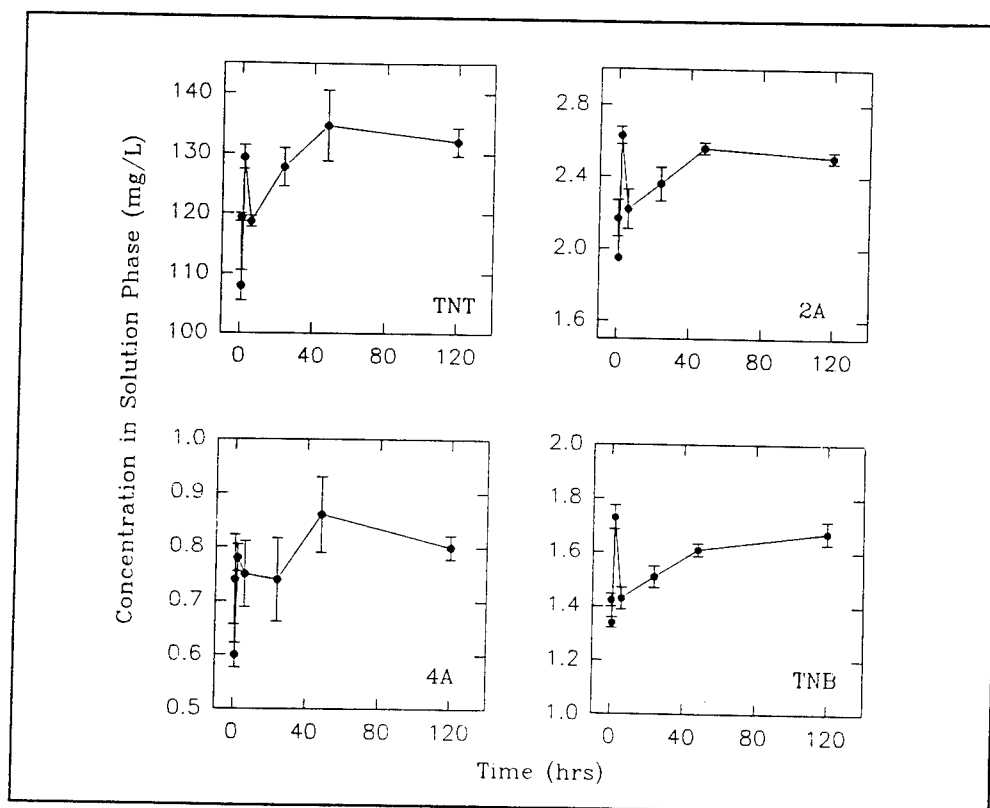


Figure 4. Desorption kinetics for TNT and three of its transformation products (2A, 4A, and TNB) in Hastings soil. Vertical bars are standard errors of the mean of three replicates

Solution phase concentrations change very little after 24 hr (Figure 5). The solution phase concentration of TNT at steady state averaged 72.2 ± 2.85 mg/L (42.1 ± 1.67 grains/gal). The solution phase concentration of RDX remained unchanged after 24 hr at an average of 53 ± 0.43 mg/L (30.9 ± 0.25 grains/gal) (average of last three data points). This concentration is near the aqueous solubility of RDX, 59.9 ± 1.4 mg/L (34.9 ± 0.82 grains/gal) at 26.5°C (Sikka et al. 1980). Since the concentration of RDX in Crane Sifter soil was high (11,200 mg/kg; 782 grains/lb), the solution phase concentration had stabilized near saturation. The solution phase concentration of HMX increased only slightly after 24 hr. The final concentration was 5.1 ± 0.10 mg/L (2.975 ± 0.058 grains/gal), which is equal to the aqueous solubility of 5 mg/L (2.9 grains/gal) at 25°C (Glover and Hoffsommer 1973). Therefore, HMX concentration had also stabilized at saturation in the solution phase of the test. The concentration of HMX in Crane Sifter soil was 1,250 mg/kg (87.3 grains/lb).

Kinetics with hot water at 55°C . Results of desorption kinetics studies using hot water (Figure 6) yielded kinetics curves that differed from those obtained using water at ambient temperature (25°C , Figure 5). After 2 days of contact, the 55°C water temperature sustained solution phase concentrations of TNT, 4A, and TNB at higher levels than ambient temperature. At 55°C , concentrations of TNT, 4A, and TNB were 32 ± 0.34 , 14 ± 0.17 , and 11 ± 0.78 mg/L (18.67 ± 0.20 , 8.17 ± 0.10 , 6.42 ± 0.46 grain/gal, respectively). At ambient temperature, concentrations

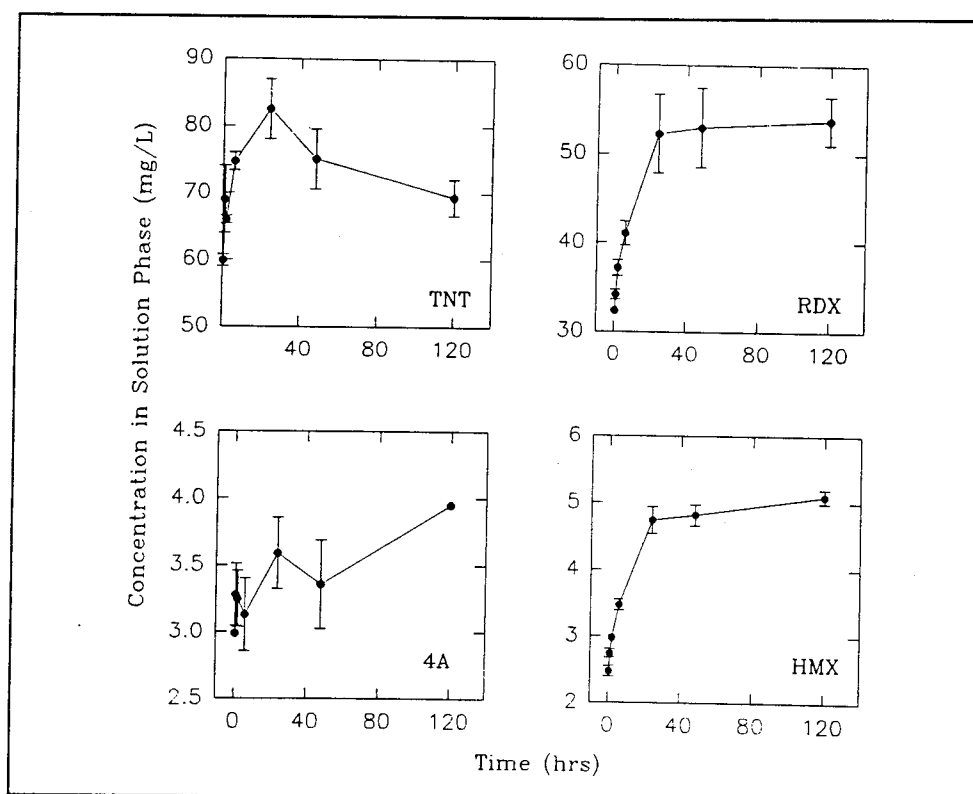


Figure 5. Desorption kinetics for TNT, RDX, 4A, and HMX in Crane Sifter soil (4 mm). Vertical bars are standard errors of the mean of three replicates

were below detection. Solution phase concentrations of TNT failed to achieve steady state during the 5-day test. Instead, concentrations decreased after 24 hr as concentrations of 4A and TNB increased. These results are consistent with transformation of TNT to these products as a result of the high temperature. These effects were much less pronounced in 40 °C tests (see results below). Although kinetics for RDX and HMX were complex, solution phase concentrations (178 ± 4.3 and 21.9 ± 3.0 mg/L (103.8 ± 2.5 and 12.8 ± 1.8 grains/gal)) at 5 days, respectively) in 55 °C tests greatly exceeded solution phase concentrations (100 ± 0.86 and 8.88 ± 0.19 mg/L (58.3 ± 0.50 and 5.18 ± 0.11 grains/gal)) at 5 days, respectively) in ambient tests.

Kinetics with hot water at 40 °C. Solution phase concentrations of TNT, RDX, and HMX in the 40 °C tests changed very little over time (Figure 6). The average concentration of TNT over time was 110 ± 10 mg/L

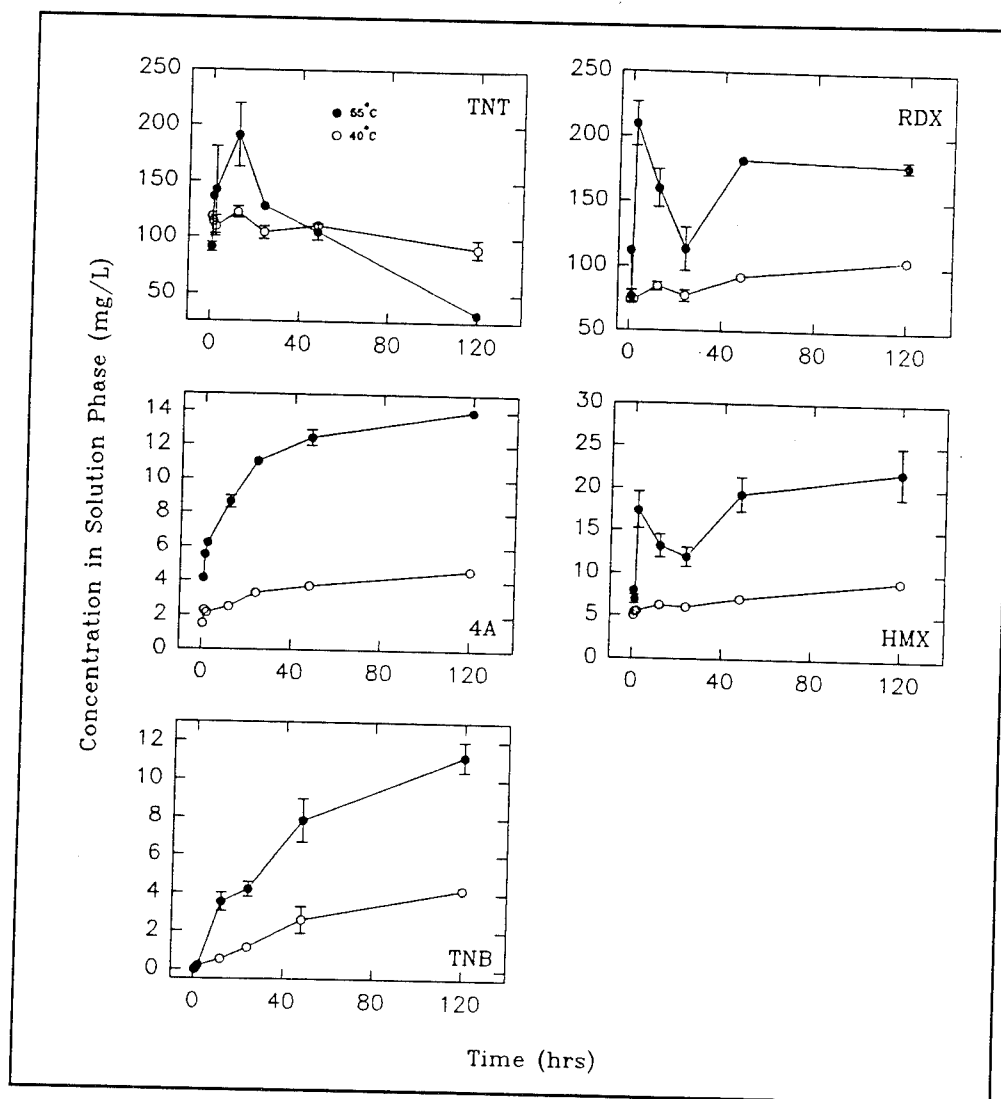


Figure 6. Desorption kinetics for TNT, RDX, HMX, 4A, and TNB in Crane Sifter soil (4 mm) challenged with water at 55 and 40 °C. Vertical bars are standard errors of the mean of three replicates

Table 3
Main Solution Phase Concentration of Contaminants Exhibiting Vertical Isotherms (mg/L)

Contaminant	Soil	Challenging Solution	Mean	Standard Error
TNT	Hastings	Water	114	7.16
		Alfonic	218	10.0
		Tween	235	5.35
	Weldon Springs	Water	119	1.12
		Alfonic	195	3.68
		Tween	235	5.35
TNB	Weldon Springs	Water	1.63	0.60
RDX	Crane Sifter	Water	47.5	0.95
		Tween	104	5.03
HMX	Crane Sifter	Water	3.84	0.15
		Alfonic	8.45	0.32
		Tween	11.0	0.29

(64.2 ± 5.8 grains/gal). This value agrees with the solution phase concentration of TNT found in TNT isotherms with other soils at ambient temperature (Table 3). Average solution phase concentration of RDX and HMX over time were 83 ± 12 and 6.3 ± 1.4 mg/L (48 ± 7 and 3.7 ± 0.8 grains/gal), respectively. These values are higher than solution phase concentrations found at ambient temperature in other soils, but lower than concentrations with surfactants (Table 3). These results suggest that water at 40°C is less effective than surfactants in increasing RDX and HMX solution phase concentration. Solution phase concentrations of 4A and TNB at 40°C continued to increase rather than leveling off. Either more TNT is mobilized from the soil phase over time, or transformation of TNT increases over time.

Kinetics with Alfonic. After 3 days, solution phase concentrations of TNT in Alfonic desorption kinetics tests had dropped to 3.11 mg/L (1.81 grains/gal) and solution phase concentrations of 4A had dropped below the detection limit (0.25 mg/L (0.15 grains/gal)) (Figure 7). This result suggests that both compounds were being transformed, degraded, or conjugated to the soil during the first 3 days of the test. Similar, though more complex, behavior was observed for RDX and HMX. Concentrations of RDX dropped from 168 mg/L (98 grains/gal) at 24 hr to about 96 mg/L at 96 hr, which is nearly twice aqueous solubility (45 to 60 mg/L (26 to 35 grains/gal), varies with source; Banerjee, Yalkousky, and Valvani 1980; Sikka et al. 1980; Spalding and Fulton 1988). Steady state was not achieved until 4 days. Concentrations of HMX, with the exception of the inexplicable drop below detection at 3 days, were fairly stable around 8 mg/L (4.7 grains/gal) beginning at 2 days. However, the last two data points suggest a slight increase. Solution phase concentrations of HMX in Alfonic were typically about 1.5 times its aqueous solubility of 5 mg/L (2.9 grains/gal).

Kinetics with Tween. The TNT and 4A kinetics curves with Tween in Crane Sifter soil were very similar to curves with Alfonic (Figure 8).

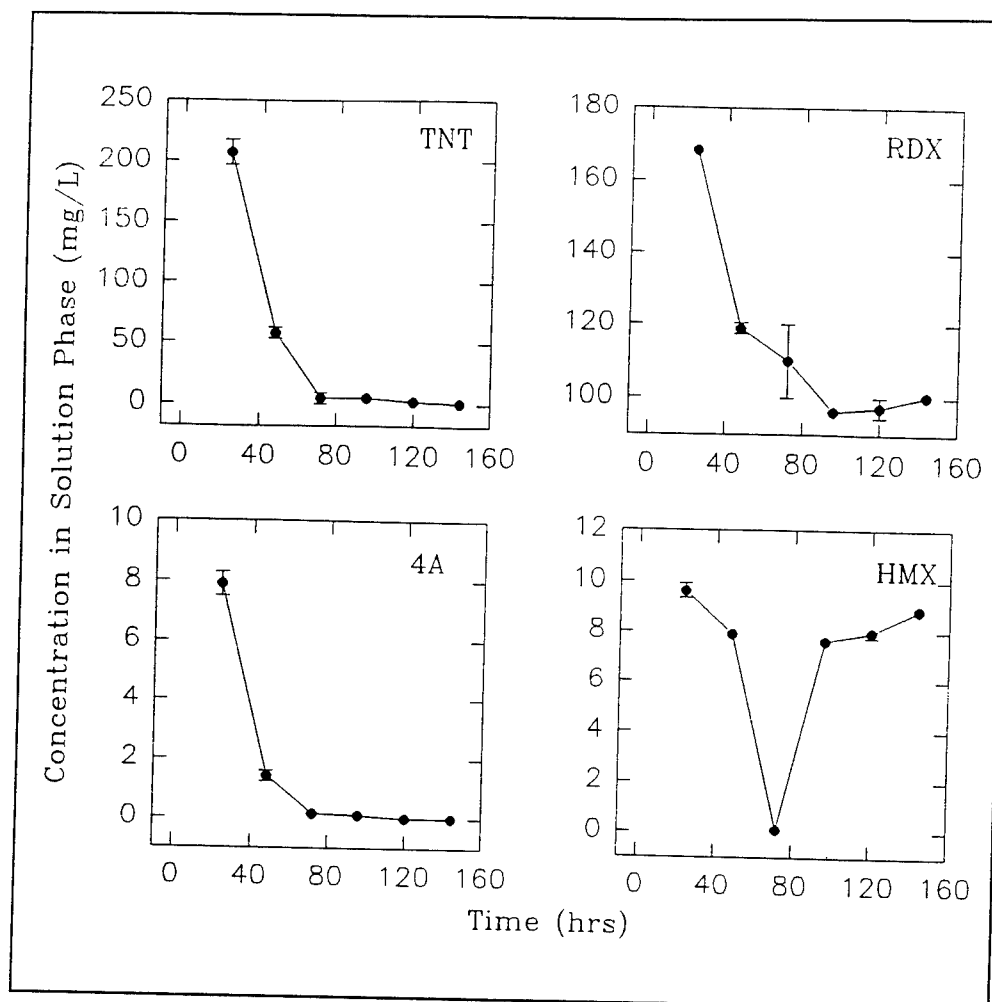


Figure 7. Desorption kinetics for TNT, RDX, 4A, and HMX in Crane Sifter soil (4 mm (0.16 in.)) challenged with Alfonic. Vertical bars are standard errors of the mean of three replicates

The solution phase concentration of TNT dropped from 175 ± 21.1 mg/L (102 ± 12.3 grains/gal) at 24 hr to less than detection limit (0.20 mg/L) (0.12 grains/gal) at 48 hr. The solution phase concentration of 4A dropped from 4.26 ± 0.188 mg/L (2.48 ± 0.11 grains/gal) at 24 hr to less than the detection limit (0.20 mg/L) (0.12 grains/gal) at 48 hr. Solution phase concentrations changed very little after 48 hr. Solution phase concentration of RDX, except for the drop to detection limit at 48 hr, averaged 96.84 ± 7.11 mg/L (56.49 ± 4.15 grains/gal). This value is the same as the steady state value determined with Alfonic. Except for the drop to detection limit at 48 hr, solution phase concentration of HMX averaged 10.35 ± 0.69 mg/L (6.04 ± 0.402 grains/gal). This value agrees well with the average steady state concentration of HMX in solution phase with Alfonic.

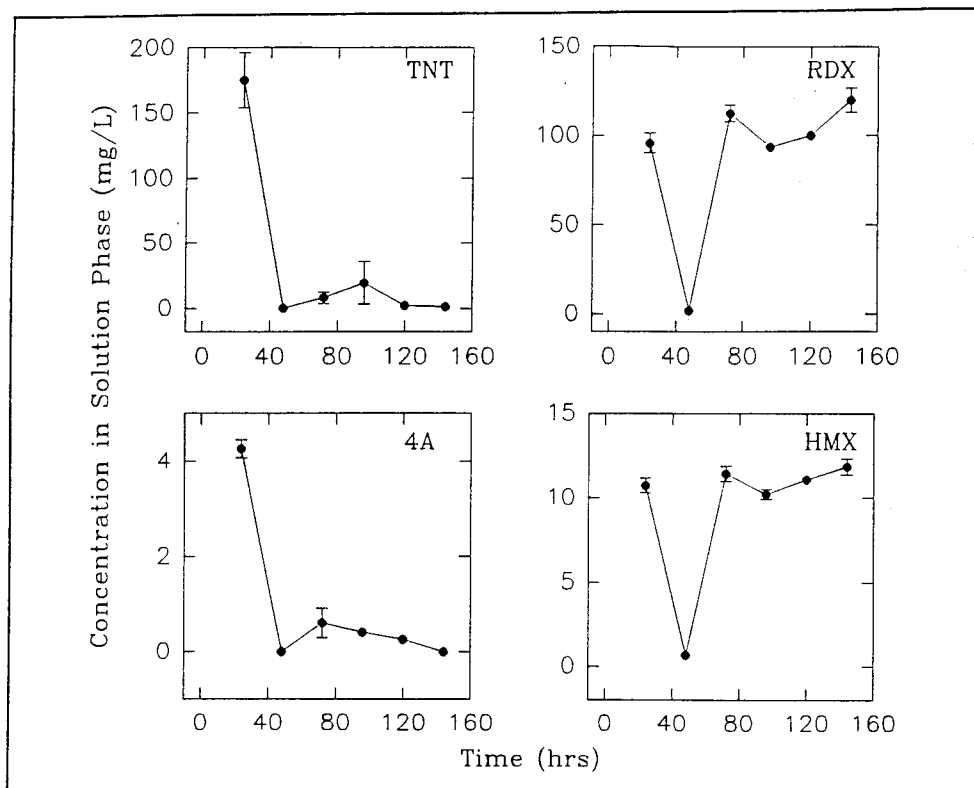


Figure 8. Desorption kinetics for TNT, RDX, 4A, and HMX in Crane Sifter soil (4 mm (0.16 in.)). Vertical bars are standard errors of the mean of three replicates

Crane 1.5 soil

Initially, kinetics data for Crane 1.5 were determined on soil inadvertently sieved to 4 mm (4,000 microns, 0.16 in.) rather than 2 mm (2,000 microns, 0.08 in.). For comparison, another kinetics test was conducted at 1, 24, and 120 hr with soil sieved to 2 mm (2,000 microns, 0.08 in.). Concentrations of RDX were comparable at 1 hr (3.4 ± 0.31 and 3.7 ± 0.16 mg/L (1.98 ± 0.18 and 2.16 ± 0.93 grains/gal) for 4- and 2-mm (4,000 microns, 0.16 in. and 2,000 microns, 0.08 in. soils, respectively (Figure 9)). However, at 24 hr the concentration in the solution phase of the 2-mm (2,000 micron, 0.08 in.) soil test was 1.5 times higher than in the 4-mm (2,000 microns, 0.08 in.) soil. Concentration at 120 hr was nearly ten times higher with 2-mm (2,000-microns, 0.08 in.) than with 4-mm (4,000 microns, 0.16 in.) soil. Since organic contaminants tend to be associated with the finer particles in soils, the concentration of each of the explosives was higher in the 2-mm (2,000-microns, 0.08 in.) than in the 4-mm (4,000-microns, 0.16 in.) soil. Therefore, higher solution phase concentrations during desorption may be a reflection of these concentration differences. However, the greater surface area of the 2-mm (2,000-microns, 0.08 in.) soil would also allow more intimate contact between solution and soil resulting in greater solution phase concentrations. The 4-mm (4,000 microns, 0.16 in.) and 2-mm (2,000 microns, 0.08 in.) soil results for TNT and HMX did not differ significantly.

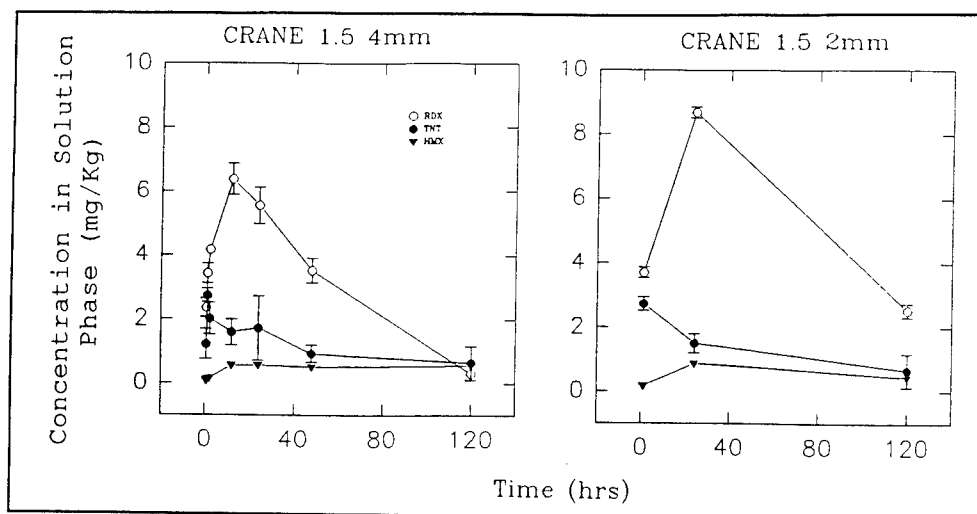


Figure 9. Desorption kinetics for RDX, TNT, and HMX in Crane 1.5 soil sieved to 4 and 2 mm (4,000 and 2,000 microns, 0.16 and 0.08 in.). Vertical bars are standard errors of the mean of three replicates

The desorption kinetics curve for RDX increased until 12 hr, then decreased steadily until the end of the 5-day test period, when the solution phase concentration was 0.76 ± 0.44 (0.44 ± 0.26 grains/gal) and 2.5 ± 0.21 (1.46 ± 0.12 grains/gal) mg/L in the 4-mm (4,000 microns, 0.16 in.) and 2-mm (2,000 microns, 0.08 in.) soils, respectively. Desorption kinetics curves for TNT decreased after 24 hr to steady state with a solution phase concentration near zero. The desorption kinetics curve for HMX increased until 12 hr at which time steady state at a low solution phase concentration (0.47 ± 0.07 mg/L (0.27 ± 0.04 grains/gal)) was reached. No TNT transformation products were detected in desorption kinetics tests with Crane 1.5 soil. If transformation of such low concentrations of TNT were occurring, concentrations of products would likely have been below detection limits.

Sequential Desorption

Desorption isotherms for TNT

Sequential desorption of the two soils with the highest initial TNT concentration, Hastings and Weldon Springs (Table 1), resulted in vertical isotherms when water and the two surfactant solutions were used to challenge the soils (Figure 10). Isotherms are vertical because each challenging solution became saturated with TNT. The mean solution phase concentration of TNT in aqueous tests (Table 3) is very near the aqueous solubility of 130 mg/L (75.8 grains/gal) reported by Gibbs and Popolato (1980). Vertical isotherms at the aqueous solubility of the contaminant can be attributed to solubilization of free product from the soil matrix. Each aqueous challenge of the Hastings and Weldon Springs soils resulted in saturation

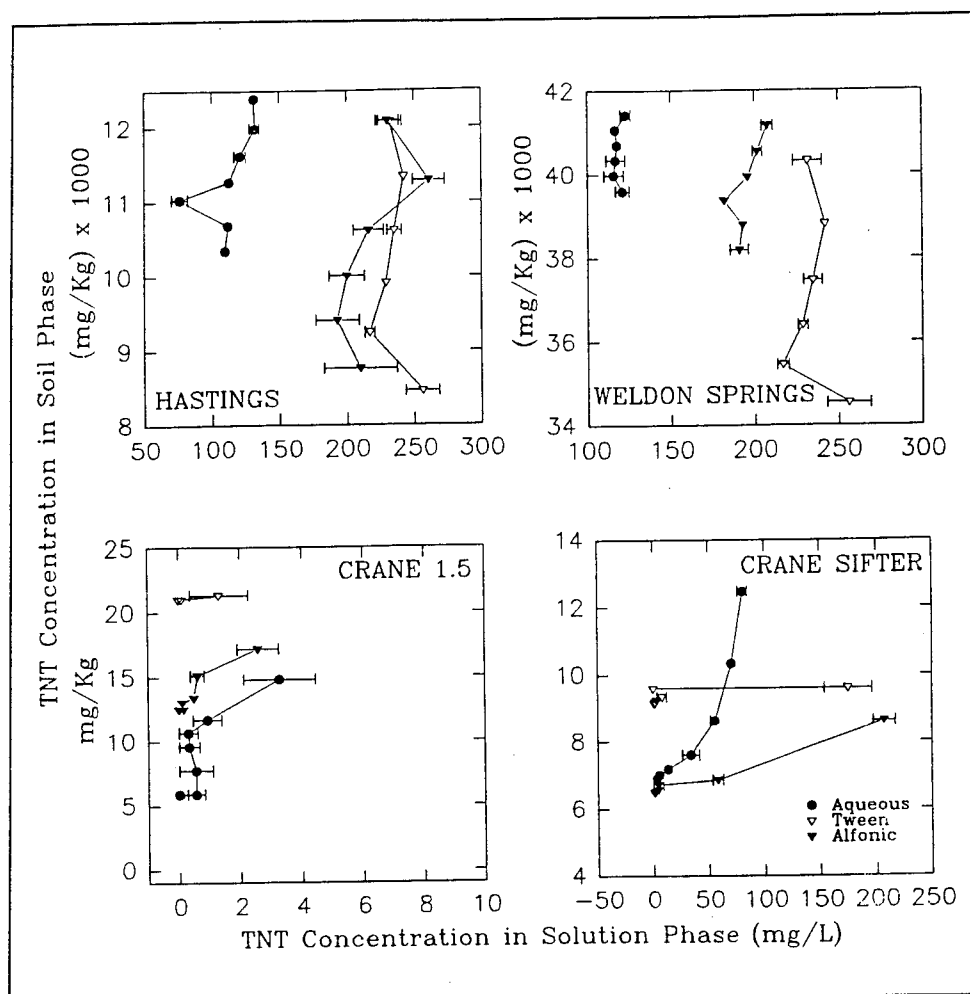


Figure 10. Sequential desorption isotherms of TNT in four explosives-contaminated soils (Hastings, Weldon Springs, Crane Sifter, and Crane 1.5). Isotherms were generated by challenging contaminated soils with water and two surfactant solutions in a 1:4 soil-to-water ratio. TNT concentrations in the solution phase were measured by high performance liquid chromatography (HPLC). Concentrations in the soil phase were determined by difference. Horizontal bars are standard errors of the mean of three replicates

of the solution phase. In such soils, the free product acts as a continuous source of contaminant. As free product is exhausted by solubilization, concentration in the solution phase is governed by desorption from soil solids. An example of this can be seen in Crane Sifter soil, which had a lower soil concentration of TNT than Hastings and Weldon Springs soils. Initial aqueous challenges resulted in a vertical isotherm, but as the free product was exhausted, partitioning between soil solids and the solution phase produced a more typical desorption isotherm (Figure 10). In Hastings and Weldon Springs soils TNT concentrations were so high that the free product was not exhausted even after seven aqueous challenges.

Vertical plots can also be explained in terms of the linear isotherm model:

$$q = K_d C \quad (1)$$

where q is the soil concentration (milligrams per kilogram; grains per pound), C is the solution phase concentration (milligrams per liter; grains per gallon), and K_d is the distribution coefficient (liters per kilogram; gallons per pound). Vertical isotherms would be expected for any compound when the soil concentration of the compound greatly exceeds the distribution coefficient multiplied by the aqueous solubility. In the current experimental design, the soil contains sufficient TNT to act as a constant source of TNT for the sequential leaching steps. Based on the range of linear K_d values reported for TNT with 16 different soils (minimum 2.3 and maximum 11.0; Pennington and Patrick 1990) and the experimental design used in these sequential desorption experiments (1:4 soil-to-water ratio), Equation 1 would predict vertical isotherms for soils having TNT concentrations in the range of 1,196 to 5,720 mg/kg (83.5 to 399.6 grains/lb) or greater. Initial concentrations of TNT in Hastings, Weldon Springs and Crane Sifter soils were 12,800, 41,800, and 1,495 mg/kg (894, 2,920, and 104 grains/lb), respectively (Table 1). Results presented in Figure 10 are consistent with those predicted by Equation 1.

Both surfactants increased TNT solubility significantly in Hastings and Weldon Springs soils (Table 3, Figure 10). Solution phase TNT concentrations in Tween were the same in both soils. Furthermore, values with Tween were consistently higher than values with Alfonic in both soils. With Alfonic, solution-phase TNT concentrations were slightly higher in the Weldon Springs than in Hastings.

Sequential desorption of the soil lowest in initial TNT concentration, Crane 1.5, resulted in isotherms having two distinct slopes; the initial desorption slope, and a vertical portion resulting from solution phase concentrations near detection limits, i.e. little or no additional TNT was leached from the soil in the final challenges (Figure 10). Differences between TNT concentrations in the solution phase of aqueous and surfactant challenges did not differ significantly.

Linear regression analysis of the aqueous isotherm of TNT in Crane Sifter soil (Figure 10) resulted in a slope of 6.16, which is consistent with K_d data reported in the literature (Pennington and Patrick 1990). The solution phase TNT concentration in the first Alfonic challenge (207 ± 10 mg/L) was consistent with the TNT solubility in the surfactant as demonstrated in the Hastings (218 ± 10 mg/L (127 ± 5.8 grains/gal)) and Weldon Springs (195 ± 3.68 mg/L (114 ± 2.15 grains/gal)) soils (Table 3). The TNT/Tween isotherm is essentially horizontal with all but one point clustered at the origin of the x-axis. Apparently, Tween exhausted its potential for removing TNT from Crane Sifter soil in the first Tween challenge. The solution phase TNT concentration in the first challenge was 175 mg/L (102 grains/gal). Saturation of this solution with TNT is unlikely, since

this value is significantly below TNT concentrations observed in Tween in Hastings and Weldon Springs soils (Table 3).

Although surfactants generally increased solution phase concentrations of TNT in initial challenges, surfactants were less effective than water in reducing the concentrations of TNT in the soil phase of the two soils lowest in TNT concentration, Crane Sifter and Crane 1.5. In Crane Sifter, soil the final concentration of TNT in the soil was nearly the same with water and Alfonic (690 and 648 mg/kg (48 and 45 grains/lb), respectively), but was higher with Tween (914 mg/kg (63 grains/lb)) (Figure 10). In Crane 1.5 soil, solution challenge resulted in a final soil concentration of 5.91 mg TNT/kg (0.41 grains TNT/lb), while the surfactants left 12.5 and 21.0 mg TNT/kg (0.87 and 1.47 grains TNT/lb), for Alfonic and Tween, respectively. Surfactants removed no more TNT after two or three challenges. However, water, while removing less in each challenge, continued to remove TNT in every challenge. In Crane Sifter soil, a single challenge removed virtually all the TNT removed by the Tween solution. Two challenges were necessary for the Alfonic solution. These results suggest that, for soils having TNT concentrations less than approximately 1,500 mg/kg (105 grains/lb), continuous leaching with water may be more effective in removal, or mobilization, of TNT than leaching with surfactants. In highly contaminated soils, such as in Hastings and Weldon Springs soils, TNT concentrations in the soil are reduced more by surfactant solutions than by water. In both soils, reductions in soil concentrations and increases in solution phase concentrations were greater with Tween than with Alfonic.

Desorption isotherms for transformation products of TNT

2A and 4A. Sequential desorption isotherms of 2A and 4A from aqueous challenges to Hastings soil were linear (R -squares of 0.98 and 0.99, respectively, Table 4 and Figure 11) and yielded K_{ds} of 6.22 and 6.06 for 2A and 4A, respectively (Table 4). Tween and Alfonic significantly increased solubilities of both compounds in Hastings soil (Figure 11). Partition coefficients (K_{ds}) were 2.24 and 3.45 for 2A in Alfonic and Tween solutions, respectively (Table 4). Partition coefficients were 3.62 and 2.32 for 4A in Alfonic and Tween, respectively (Table 4). Lower K_{ds} with surfactant than with aqueous challenges are consistent with the increases in solubility achieved by the added surfactants.

TNB. In the soil most highly contaminated by TNT (Weldon Springs), no initial TNB was detected (Table 1). TNB was not detected in the solution phase of sequential desorption tests until the third challenge, after which concentrations declined (Figure 12). This behavior suggests destabilization of TNB from the soil or formation of TNB during testing. In Hastings soil, the aqueous isotherm of TNB was linear (R -square = 0.90) and had a K_d of 2.90 (Figure 12). The TNB isotherm was better fit by a third-order equation (R -square = 0.999). Both surfactants increased the

Table 4
Regression Parameters for Sequential Desorption Isotherms
with Water and Two Surfactants, Alfonic and Tween

Contaminant	Soil	Challenging Solution	Linear Regression		
			Intercep	Solution	R-Square
TNT	Hastings	Water	S	na	na
		Alfonic	S	na	na
		Tween	S	na	na
	Weldon Springs	Water	S	na	na
		Alfonic	S	na	na
		Tween	S	na	na
	Crane Sifter	Water	627	6.16	0.86
		Alfonic	650	0.997	0.98
	Crane 1.5	Tween	D	na	na
		Water	D	na	na
		Alfonic	D	na	na
		Tween	D	na	na
2A	Hastings	Water	6.28	6.22	0.98
		Alfonic	-1.28	2.24	0.97
		Tween	-6.55	3.45	0.71
4A	Hastings	Water	20.3	6.06	0.99
		Alfonic	7.56	3.62	0.944
		Tween	20.5	2.32	0.867
TNB	Hastings	Water	24.4	2.90	0.90
		Alfonic	0.016	6.424	0.931
		Tween	7.87	5.63	0.934
	Weldon Springs	Water	124	4.38	0.26
		Alfonic	14.0	5.15	0.923
		Tween	22.5	3.74	0.951
RDX	Crane Sifter	Water	S	na	na
		Alfonic	D	na	na
		Tween	S	na	na
	Crane 1.5	Water	D	na	na
		Alfonic	D	na	na
		Tween	D	na	na
HMX	Crane Sifter	Water	S	na	na
		Alfonic	S	na	na
		Tween	S	na	na
	Crane 1.5	Water	D	na	na
		Alfonic	D	na	na
		Tween	D	na	na
S Vertical isotherm resulting from solution phase saturation in each desorption cycle D Rapid depletion of leachable contaminant resulting in isotherm exhibiting two distinct slopes, one of which was vertical na Not applicable					

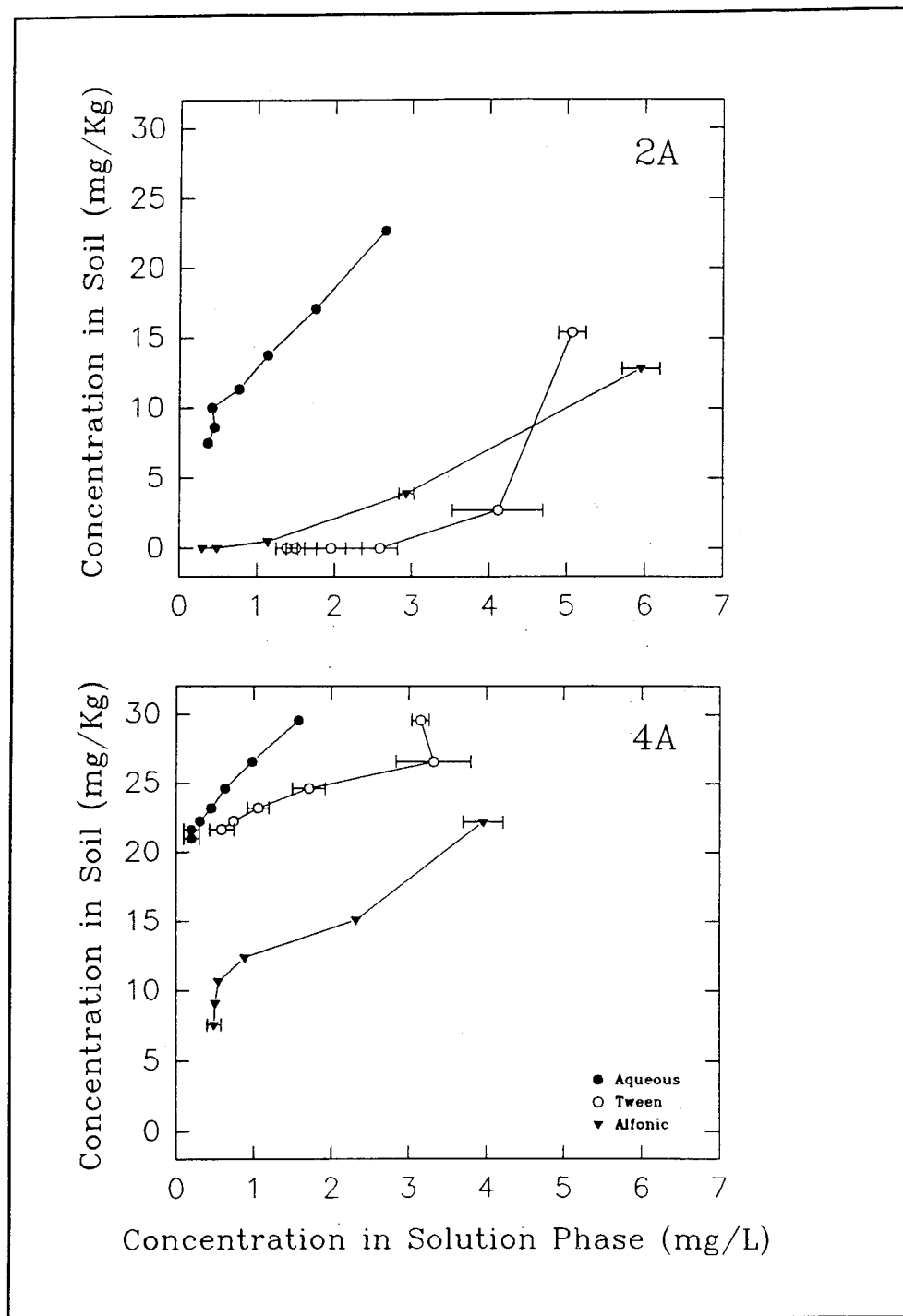


Figure 11. Sequential desorption isotherms of two transformation products 2A and 4A, in an explosive-contaminated soil from Hastings East Industrial Park. Isotherms were generated by challenging contaminated soil with water and two surfactant solutions in a 1:4 soil-to-water ratio. Contaminant concentrations in the solution phase were measured by HPLC. Concentrations in the soil phase were determined by difference. Horizontal bars are standard errors of the mean of three replicates

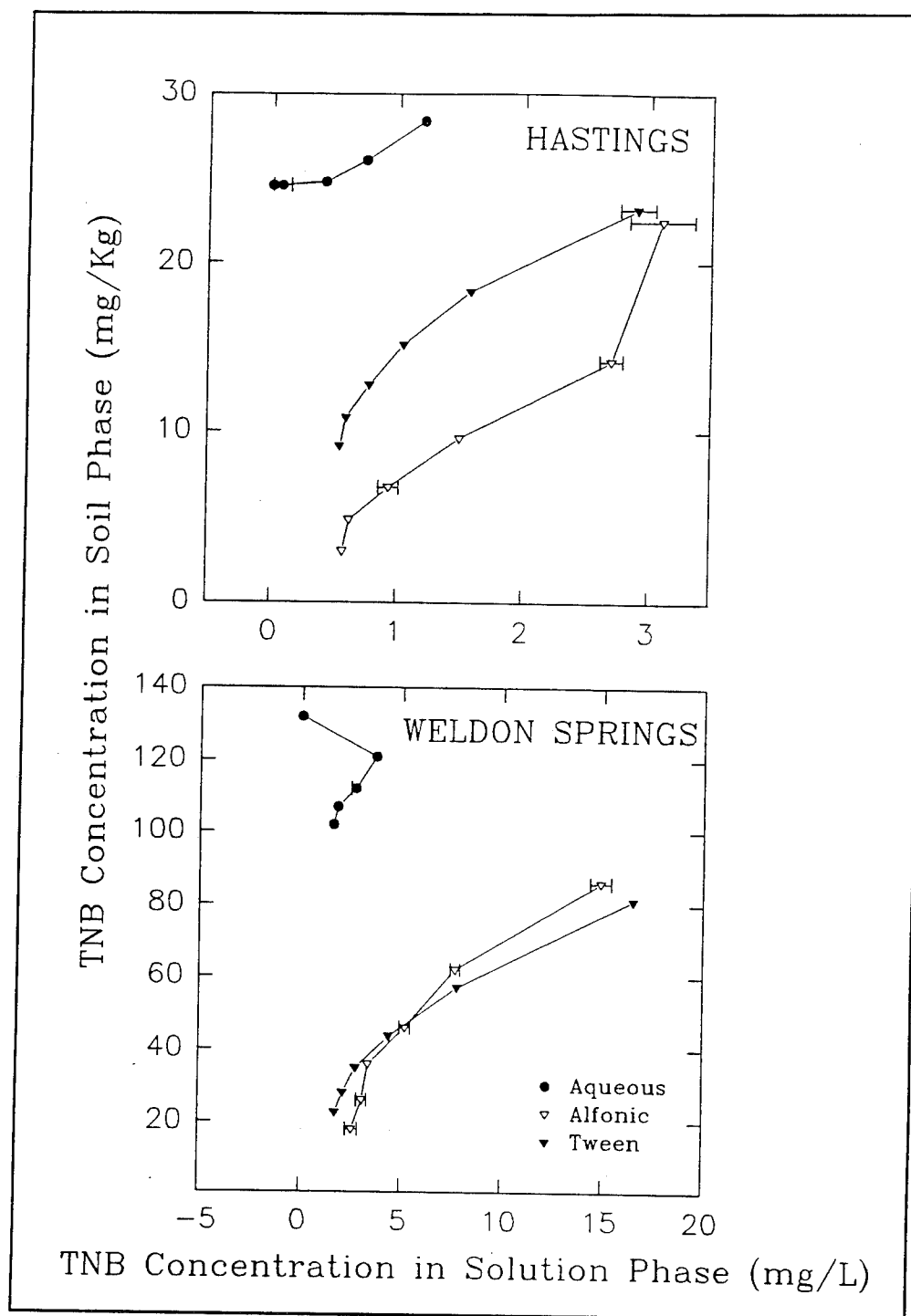


Figure 12. Sequential desorption isotherms of TNB, a photodecomposition product of TNT, in two explosive-contaminated soils, Hastings and Weldon Springs. Isotherms were generated by challenging contaminated soils with water and two surfactants in a 1:4 soil-to-water ratio. Concentrations in the solution phase were measured by HPLC. Concentrations in the soil phase were determined by difference. Horizontal bars are standard errors of the mean of three replicates

amount of TNB in the solution phase in both soils (Figure 12). This result is consistent with the findings of Gunnison et al. (in preparation) in which Tween in combination with nutrients and a cometabolite (toluene) increased formation of TNB. Their results suggest biotic and/or abiotic transformation of TNT to TNB in the presence of the amendments. The TNB may also be more strongly adsorbed than the other analytes and may require surfactants for desorption. Isotherms for TNB in both surfactant solutions with both soils were linear (R-Square 0.9, Table 4). Partition coefficients (K_{ds}) for TNB in surfactants were slightly higher than for 2A and 4A surfactant challenges (Table 4). Alfonic K_{ds} were slightly higher than Tween K_{ds} . Values of TNB K_{ds} were slightly higher for both surfactant solutions with the Hastings than with the Weldon Springs soil.

RDX. Only two soils exhibited initial concentrations of RDX, Crane Sifter and Crane 1.5 (Table 1). In Crane Sifter soil, sequential aqueous challenge resulted in a vertical isotherm (Figure 13). Surfactants significantly increased solution phase concentrations, resulting in nearly vertical isotherms with concentrations more than twice those generated by challenging the soil with water alone. Crane 1.5, which had a relatively low initial concentration of RDX, exhibited two-slope isotherms for aqueous and surfactant challenges as described for the same soil with TNT. If data points near detection limits are eliminated from the Crane 1.5 data set, linear regression analysis of the aqueous and Tween isotherms results in K_{ds} of 0.674 (R-Square = 0.99) and 0.653 (R-Square=1.0), respectively.

HMX. Only Crane Sifter and Crane 1.5 soils exhibited initial concentrations of HMX (Table 1). In the more contaminated of the two soils, Crane Sifter, aqueous and surfactant isotherms were vertical (Figure 14). Aqueous solubility of HMX is 5 mg/L (2.9 grains/gal) (Glover and Hoffsommer 1973). This value is in good agreement with the mean solution phase concentration of aqueous challenges, 3.84 ± 0.150 mg/L (2.24 ± 0.088 grains/gal) (Table 3). Both surfactants significantly increased solution phase concentrations of HMX, but concentrations with Tween were greater than with Alfonic (Table 3). With Crane 1.5 soil, solution phase concentrations of HMX were extremely low for aqueous and surfactant challenges, less than 2 mg/L (1.2 grains/gal). Therefore, these isotherms primarily reflect variability about analytical detection limits. No K_d with aqueous challenge was determined for HMX, since one of the soils, Crane Sifter, exhibited concentrations that were too high, 1,250 mg/kg (87 grains/lb), and the other soil, Crane 1.5, exhibited concentrations that were too low, 4.8 mg/kg (0.34 grains/lb), which generated a horizontal isotherm (Figure 14).

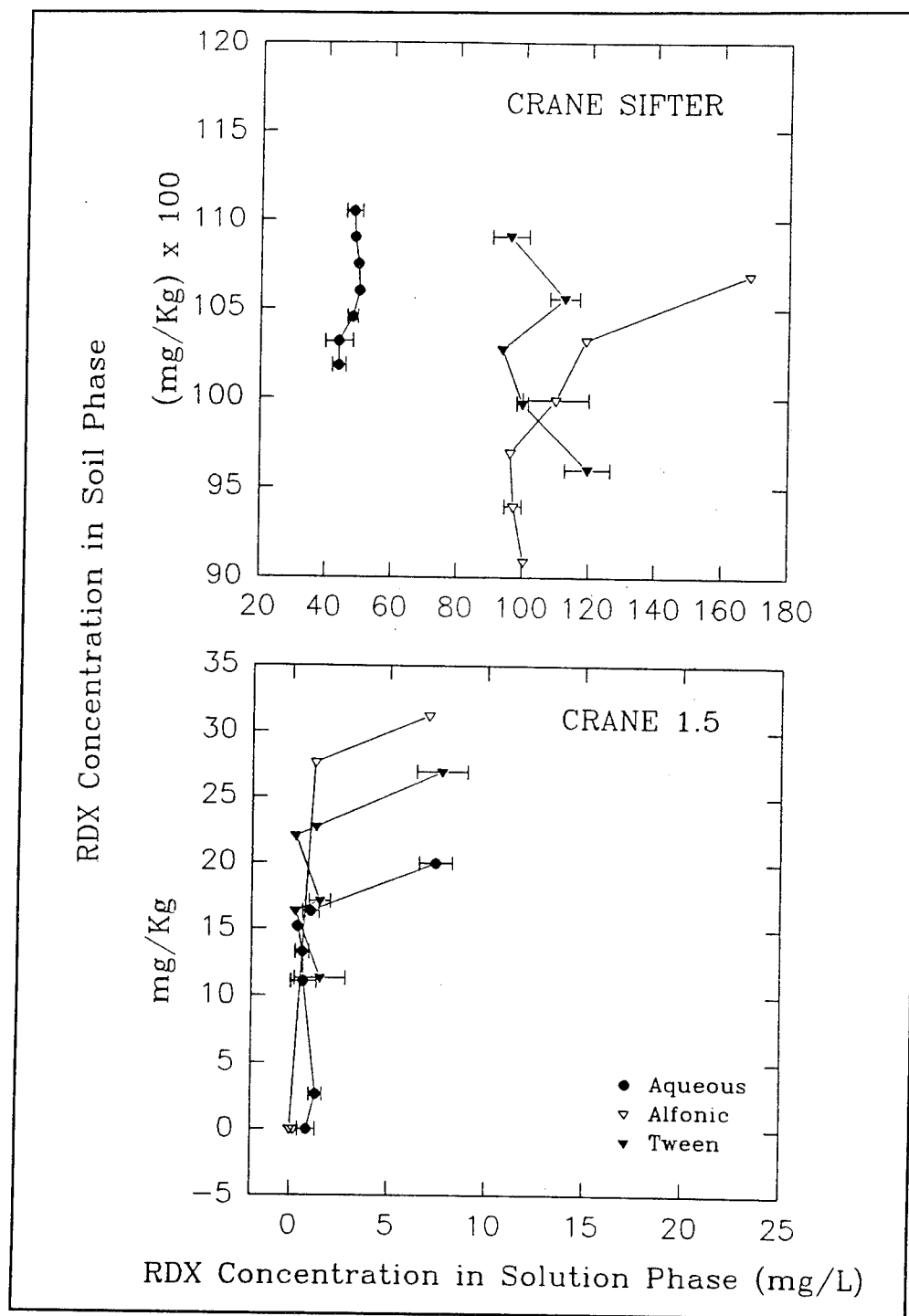


Figure 13. Sequential desorption isotherms of RDX in two explosive-contaminated soils, Crane Sifter and Crane 1.5. Isotherms were generated by challenging contaminated soils with water and with two surfactants in a 1:4 soil-to-water ratio. Concentrations in the solution phase were measured by HPLC. Concentrations in the soil phase were determined by difference. Horizontal bars are standard errors of the mean of three replicates

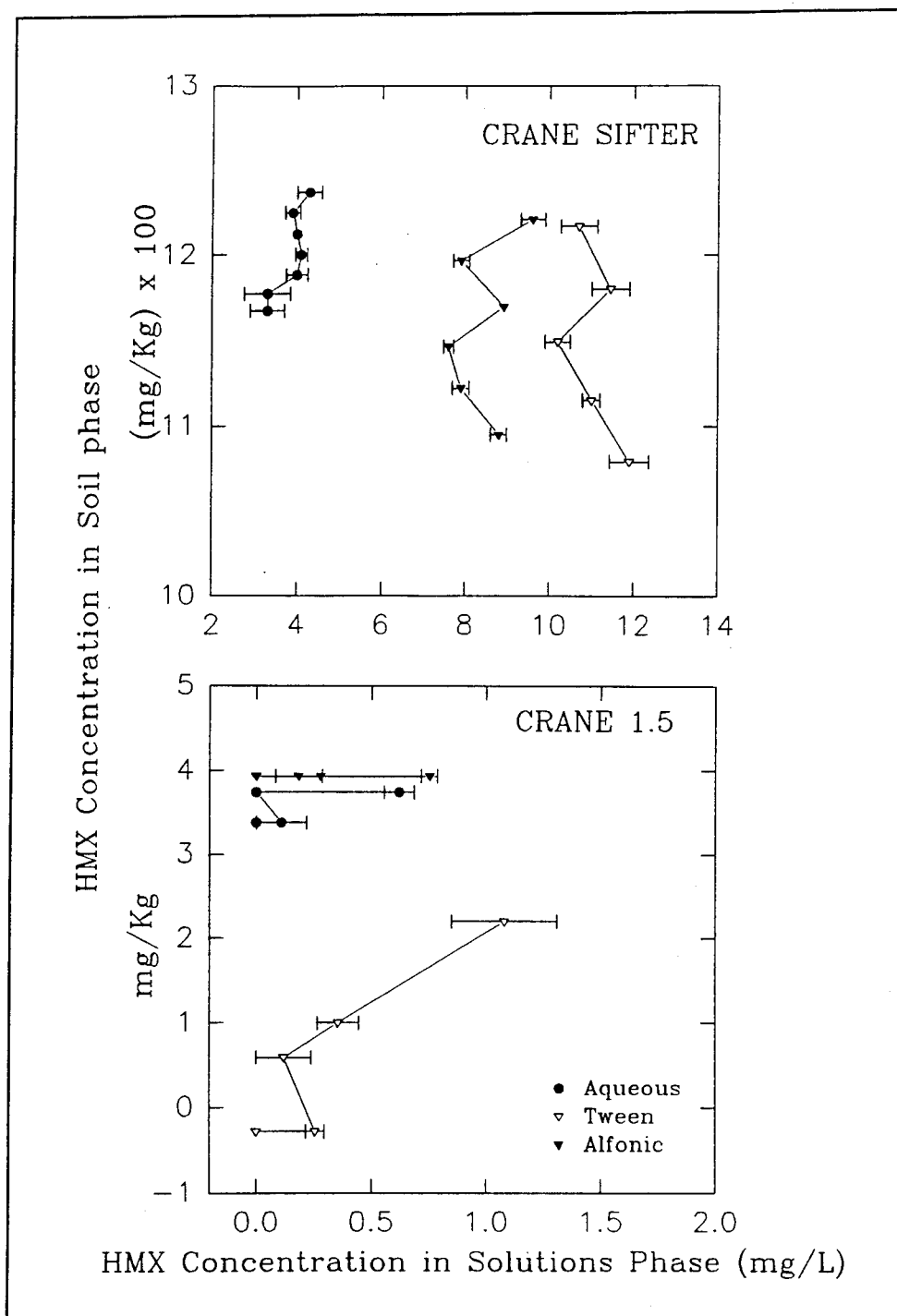


Figure 14. Sequential desorption isotherms of HMX in two explosive-contaminated soils, Crane Sifter and Crane 1.5. Isotherms were generated by challenging contaminated soils with water and with two surfactants in a 1:4 soil-to-water ratio. Concentrations in the solution phase were measured by HPLC. Concentrations in the soil phase were determined by difference. Horizontal bars are standard errors of the mean of three replicates

Column Tests

TNT and transformation products of TNT

Elution curves for TNT (2A and 4A) are shown in Figure 15. Following the onset of flow, initial effluent concentrations of TNT, 2A, and 4A were approximately 0.20, 0.11, and 0.14 mg/L (0.12, 0.061, and 0.082 grains/gal), respectively. (Detection limits for each analyte in column eluate was 0.02 mg/L (0.012 grains/gal).) Maximum TNT concentration occurred after approximately 0.6 pore volumes were eluted, rather than as the initial point of the elution curve. TNT concentrations then declined in an irregular manner to a low of approximately 0.016 mg/L (9.33×10^{-3} grains/gal) at approximately 5.3 pore volumes eluted. TNT concentrations then increased to a level which remained within a range of approximately 0.10 - 0.27 mg/L up to termination of the experiment, at which time 19.1 pore volumes had been eluted. The irregular behavior may be due to flow irregularities, uneven sorption effects, or other phenomena.

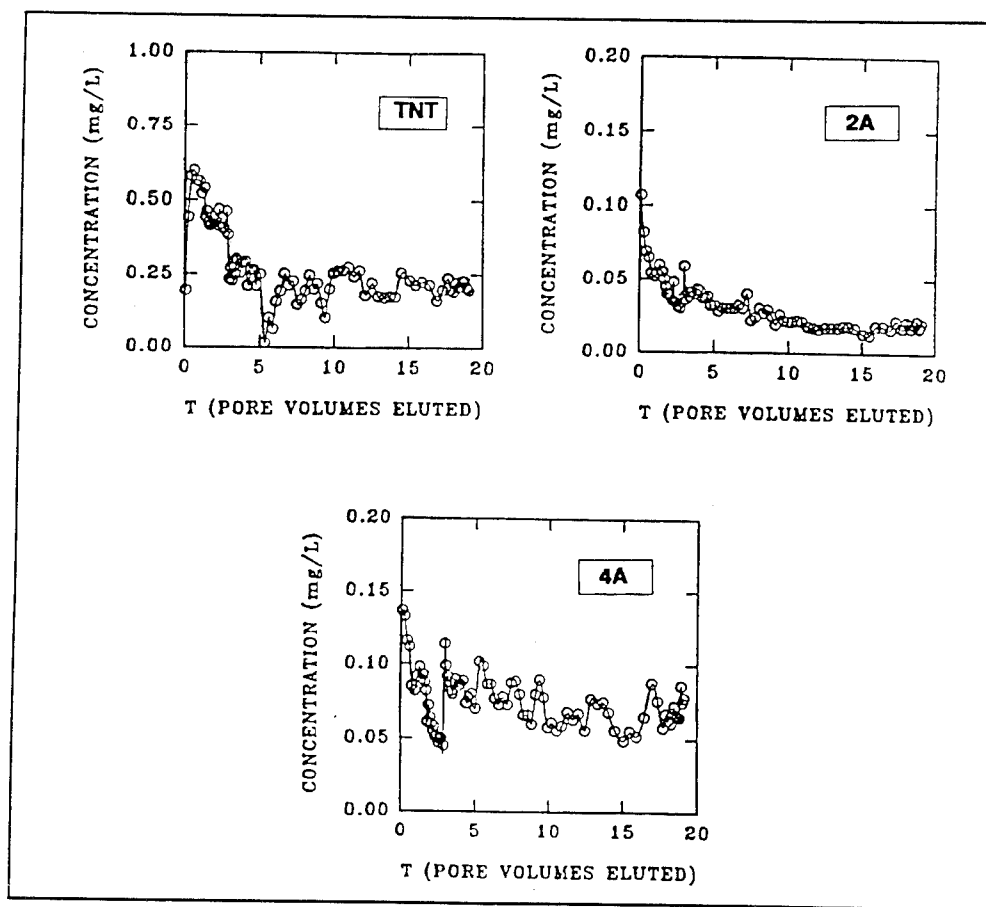


Figure 15. Elution curves for TNT, 2A, and 4A from Crane 1.5 soil column

Concentrations of 2A (Figure 15) tended to decline continuously from the initial high of 0.11 mg/L (0.063 grains/gal) to a level that remained relatively steady between 0.016 - 0.022 mg/L (9.3 ± 10^{-3} - 0.013 grains/gal). Concentrations of 4A declined to a low of 0.045 mg/L (0.026 grains/gal) at approximately 3 pore volumes eluted and then increased abruptly to about 0.12 mg/L (0.07 grains/gal) (Figure 15). The general trend over the remaining pore volumes eluted was a rather irregular, gradual decline to a range of concentrations between 0.05 - 0.10 mg/L (0.029 - 0.058 grains/gal).

Figures 16a and 16b show the interrelationship of TNT, 2A, and 4A concentrations over the first portion and the entire leaching experiment, respectively. Figure 16a shows a steady state plateau over 1 pore volume elution for TNT, 2A, and 4A. This plateau represents displacement of the equilibrated pore water in the column. Figure 16b shows that sharp declines in TNT concentration are accompanied by small increases in 4A

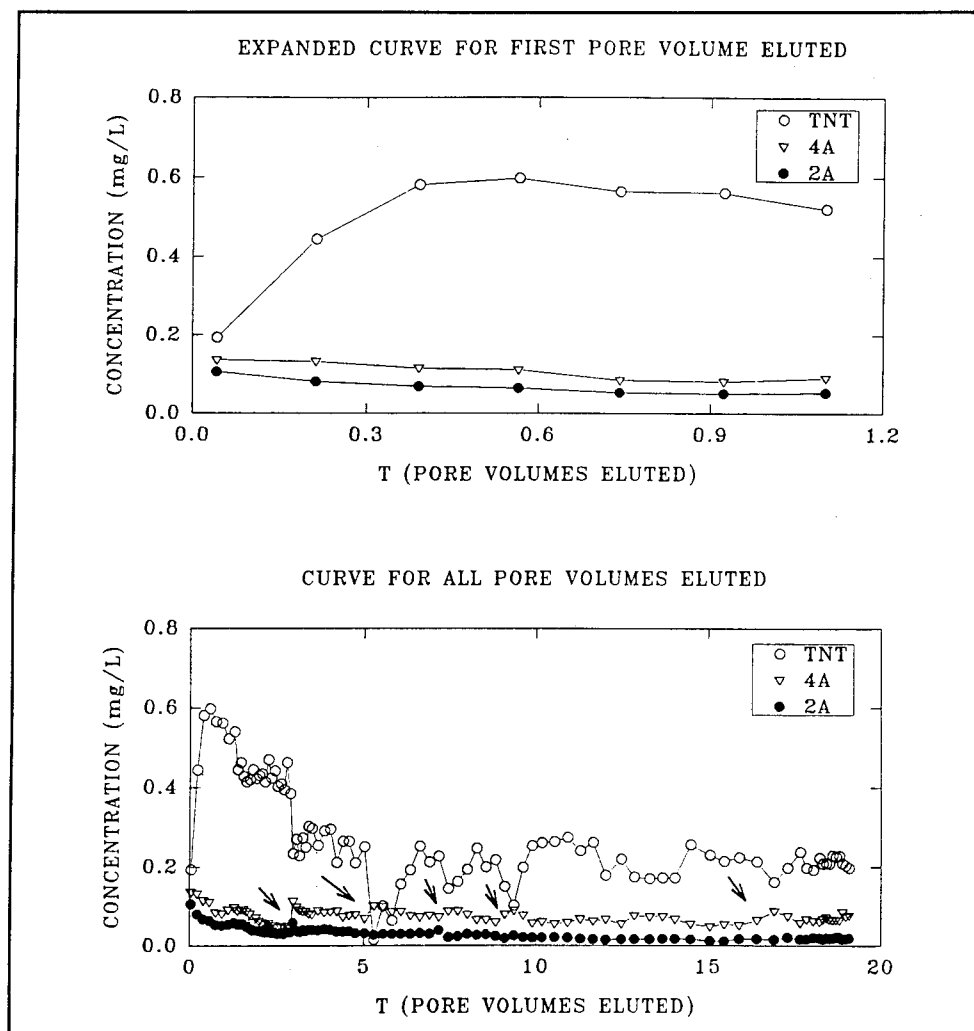


Figure 16. Expanded correspondence curve for TNT, 2A, and 4A in the first pore volume eluted (upper graph) and the curve for all pore volumes eluted (lower graph) from Crane 1.5 soil

concentrations (arrows in Figure 16b). The concentrations of 2A declined from an initial maximum and appeared to be independent of TNT and 4A concentrations. Mechanisms that could account for the correspondence between TNT and 4A include: (a) displacement of sorbed 4A as TNT adsorbs (competitive sorption), (b) adsorption of TNT followed by transformation to 4A and desorption of 4A into solution, and (c) transformation of TNT in the solution phase to 4A simultaneous with TNT adsorption.

Chemical analysis of the sectioned column following the leaching experiment revealed high soil concentrations of TNT, 2A, 4A and TNB near the column outlet (Figure 17). TNT concentrations in this portion of the sectioned column are three orders of magnitude higher than concentrations present in the soil sample analyzed prior to the leaching study. This could be due to the presence of solid phase TNT in the column. Development of a highly contaminated zone by chromatography effects is not physically possible if the soil column is initially homogeneous because chromatography is a separation technique, not a concentration technique. Thus, the sectioned soil data show that the soil column was not initially

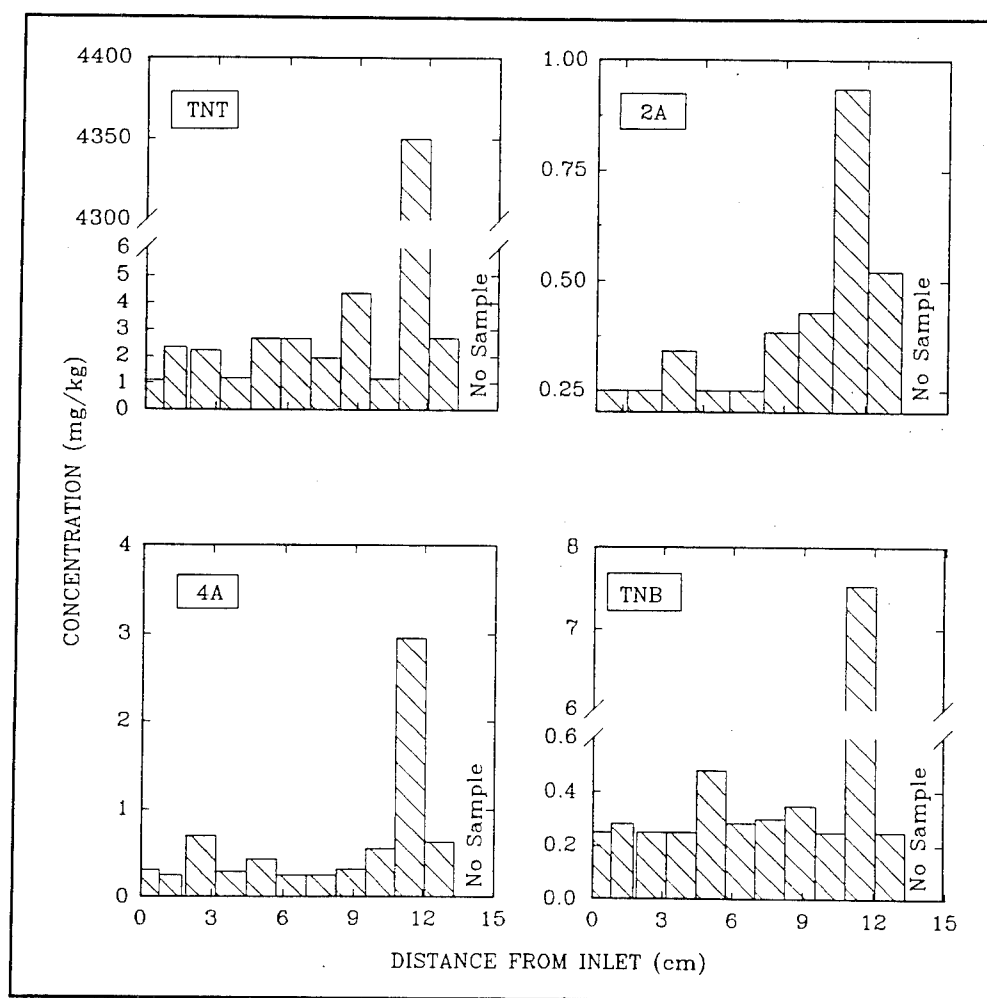


Figure 17. Residual concentrations of TNT, 2A, 4A, and TNB in Crane 1.5 soil after leaching

homogeneous and suggest the possibility of crystalline TNT in the section with the high TNT concentration. RDX and HMX were not detectable in the sectioned soil samples.

As previously discussed in the section on sequential desorption, dissolved TNT concentrations are solubility limited when soil TNT concentrations exceed 1,500 mg/kg (875 grains/lb). Since soil TNT concentrations in the 3.2-to 4.5-cm (1.28- to 1.8-in.) section of the column were greater than 1,500 mg/kg (875 grains/lb), pore water TNT concentrations in this region of the column should be solubility limited. The TNT elution curve indicated dissolution/dispersion as the processes governing dissolved TNT concentrations in the column effluent. Dissolution/dispersion accounts for the relatively steady TNT concentrations after about five pore volumes were eluted. Dissolved TNT concentrations in the effluent, however, were substantially below the solubility limit of TNT. The shape of the TNT elution curve, the dissolved TNT concentrations in the column effluent, and the TNT soil concentrations obtained after the elution experiment indicate the presence of crystalline TNT in the soil column. Hydrodynamic mixing diluted TNT concentrations in the vicinity of crystalline TNT with water at significantly lower concentrations. Mixing and dilution continued until the water reached the column outlet. Thus, TNT concentrations at the column outlet tended to hold steady as the crystal(s) continued to dissolve at a steady rate.

RDX and HMX

RDX and HMX (Figure 18) declined consistently from initial high concentrations of 2.4 and 0.677 mg/L (1.4 and 0.39 grains/gal), respectively. An irregularity exists in the HMX elution curve at approximately three pore volumes (about the same point at which 4A concentrations rose abruptly), at which HMX concentrations increased to approximately 0.100 mg/L (0.058 grains/gal) and then continued to decline as before. The one-dimensional convective-dispersive solute transport equation with equilibrium-controlled linear sorption and first order decay provided a good theoretical correspondence to the observed RDX elution curve. HMX elution is less well modeled by this equation.

The theoretical elution curves shown in Figure 18 were obtained from an analytical solution to the advection-dispersion equation with equilibrium-controlled sorption and first order decay (van Genuchten and Alves 1982). The fitted retardation coefficients ($R = 2$ for RDX and $R = 7$ for HMX) indicate low sorption. If sorption coefficients had been higher, initial RDX and HMX concentrations would have persisted longer. The fitted first-order disappearance coefficients ($u = 0.000029 \text{ sec}^{-1}$ for RDX and $u = 0.000025 \text{ sec}^{-1}$ for HMX) indicate rapid disappearance of RDX and HMX, perhaps due to biodegradation. Although a mass balance was not calculated for RDX and HMX, the areas under the curves in Figure 18 cannot account for the RDX and HMX in the soil prior to leaching. Thus, some of the RDX and HMX disappeared during column leaching.

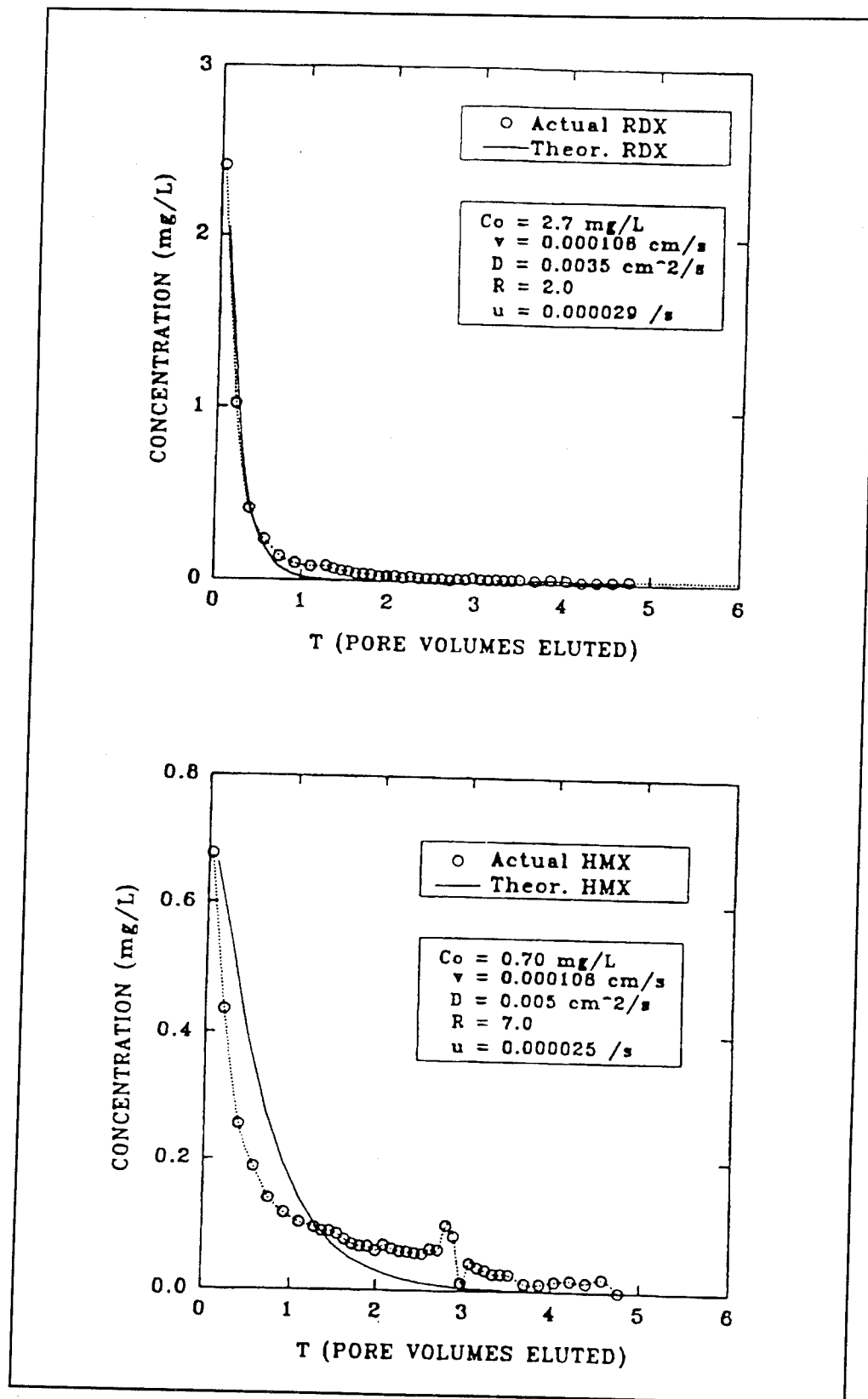


Figure 18. Elution curves of RDX and HMX from Crane 1.5 soil

Application of the disappearance coefficients obtained from curve fitting over a 35-day period (the time period of the leaching test) to the original soil RDX and HMX concentrations would predict approximately zero soil concentrations of RDX and HMX at the end of the leaching experiment. This prediction is consistent with the sectioned soil results. However, since no RDX or HMX transformation products were analyzed, it is not certain whether any identifiable products persisted.

TNB, DNB, tetryl and 2,4DNT were below detection throughout the study. Except for TNB (0.544 mg/kg (0.038 grains/oz)), these compounds were nondetectable in the soil prior to the leaching test. Thus, DNB, tetryl, and 2,4DNT were not generated during the leaching experiment. TNB did not leach in detectable quantities. These results are consistent with results of sequential desorption tests in which TNB was not detected until the third challenge, after which concentrations declined (Figure 12).

The HMX elution curve showed significant tailing. This tailing suggests that physical nonequilibrium processes such as diffusion from immobile water regions, affected leaching of HMX from this soil (Brusseau and Rao 1989). The RDX elution curve showed little tailing. The absence of tailing suggests that physical nonequilibrium processes did not affect leaching of RDX from this soil.

Several interesting comparisons of elution behavior among explosives are available from this experiment. RDX was mobile, degradable, and unaffected by physical non-equilibrium processes. HMX was also mobile and degradable, but physical non-equilibrium processes affecting HMX transport were evident. RDX and HMX showed no evidence of a residual soil component that resisted leaching. TNT persisted and was not significantly degraded. A residual TNT component persisted throughout the soil column. In addition, TNB was resistant to leaching.

For RDX and HMX, disappearance mechanisms, either biotic or abiotic processes, played a role in modeling elution curves. The TNT elution curves could not be modeled due to complicated soil interactions and chemical heterogeneities.

A desorption-resistant soil component would not be expected to present problems for remediation of RDX and HMX in this soil by pump-and-treat or in situ bioremediation technologies. However, the highly heterogeneous distribution of TNT contamination of Crane 1.5 soil and the presence of leaching-resistant soil residuals could greatly limit the effectiveness of pump-and-treat remediation by preventing sufficient and timely removal of contaminants from soil (Mercer, Skipp, and Giffin 1990; Travis and Doty 1990). Leaching-resistant soil residuals could also slow desorption, restricting microbial access to contaminants during in situ bioremediation.

4 Implications for In Situ Bioremediation

Effects of Concentration on Mobility of Explosives in Soils

Explosives potentially occupy several compartments in the soil. For example, explosives may be (a) crystallized solid (free product) heterogeneously distributed near the soil surface, (b) sorbed onto soil solids including organic matter and soil minerals, (c) associated with fine suspendable soil particles, or (d) dissolved in the soil solution. The concentration of bioavailable explosive depends upon the dynamic interactions of these compartments with water. Typically, bioavailability is assumed to be highest when concentrations in soil solution are highest. Mobility of explosives from highly contaminated soil containing crystallized solid explosive depends primarily upon the aqueous solubility of the explosive. Mobility of explosives sorbed to soil solids depends upon partitioning between solid and solution phases. If solution phases are constantly saturated by dissolution of free product, concentrations in the solution phase are determined by the aqueous solubility of the explosive rather than by partitioning. In facilitated transport, solution phase concentrations appear to exceed the aqueous solubility of the explosive because fine soil solids containing sorbed explosive become suspended in the soil solution. Characteristics of the soil, such as particle size distribution and organic carbon content, determine the potential for facilitated transport.

When TNT, RDX, and HMX concentrations in soils are high, the soil acts as a continuous source of contaminant to infiltrating water. When highly contaminated soil is in the saturated zone, bioavailability will be limited only by the aqueous solubility of the explosive. When concentrations of explosives are moderate to low, e.g. less than approximately 1,500 mg TNT/1 kg (875 grains TNT/oz) soil, partitioning between soil solid and solution phases controls solution phase concentration, and is, therefore, important to bioavailability of the explosives. Critical loadings for RDX and HMX could not be estimated from the data obtained in this study. However, partitioning theory indicates a range of 30-100 mg/kg (2.096 - 6.98 grains/oz) for both explosives.

Heterogeneities in soil contamination levels also affect bioavailability. For example, microcrystals of TNT in a soil matrix are rarely uniformly distributed. Exposure concentrations for microbes immediately adjacent to crystalline TNT will approach the solubility limit. These concentrations may inhibit microbial activity. Exposure concentrations for microbes a few millimeters distance from crystalline TNT will be governed by mass transfer effects and hydrodynamic mixing (dilution). If exposure concentrations under these conditions do not inhibit microbial degradation of TNT, degradation is controlled by biokinetic rates, dissolution rates, or mass transfer rates -- whichever are slowest.

Sorption in Three In Situ Bioremediation Scenarios

In situ biotreatment of saturated soils

For in situ biotreatment of saturated soils, nutrients, oxygen and com-etabolites are introduced into the biologically active zone (BAZ) through injection wells and solution is removed from dewatering wells (Figure 19). When concentrations of TNT in the soil exceed 1,500 mg/kg (875 grains/lb), concentrations in the moving solution will be limited by aqueous solubility, flushing rates, and microbial activity rather than by sorption. When concentrations are low in saturated soils (for example, less than 20 mg/kg (1.40 grains/lb)), surfactants may be needed to increase bioavailability of explosives. Formulation of general guidance for surfactants to increase bioavailability of TNT is given in the chart below; however, the database upon which the values are based is extremely limited.

TNT Concentration in Soil (mg/kg)	Surfactant	Remarks
>1,500	No	Solution phase concentration is limited by aqueous solubility; probably concentrations are as high as necessary for bioremediation
20 - 1,500	Maybe	Testing needed to determine efficacy of adding surfactant
<20	Yes	Solution phase concentration is limited by sorption; surfactant should enhance bioavailability

High concentrations of explosives in the mobile phase of such treatment systems may be toxic or inhibitory to the degrading microflora. Addition of surfactants, which increase the amount of explosive in solution by a factor of two or three compared to water alone, may be unnecessary. This is especially true if solution phase concentrations of explosives are already as high as microbial populations can tolerate. Data on tolerance of microflora to explosives are limited. Klausmeier, Osmon, and Walls (1973) demonstrated that fungi, yeast, actinomycetes, and gram positive bacteria grew when TNT

Saturated Zone In-situ Biotreatment

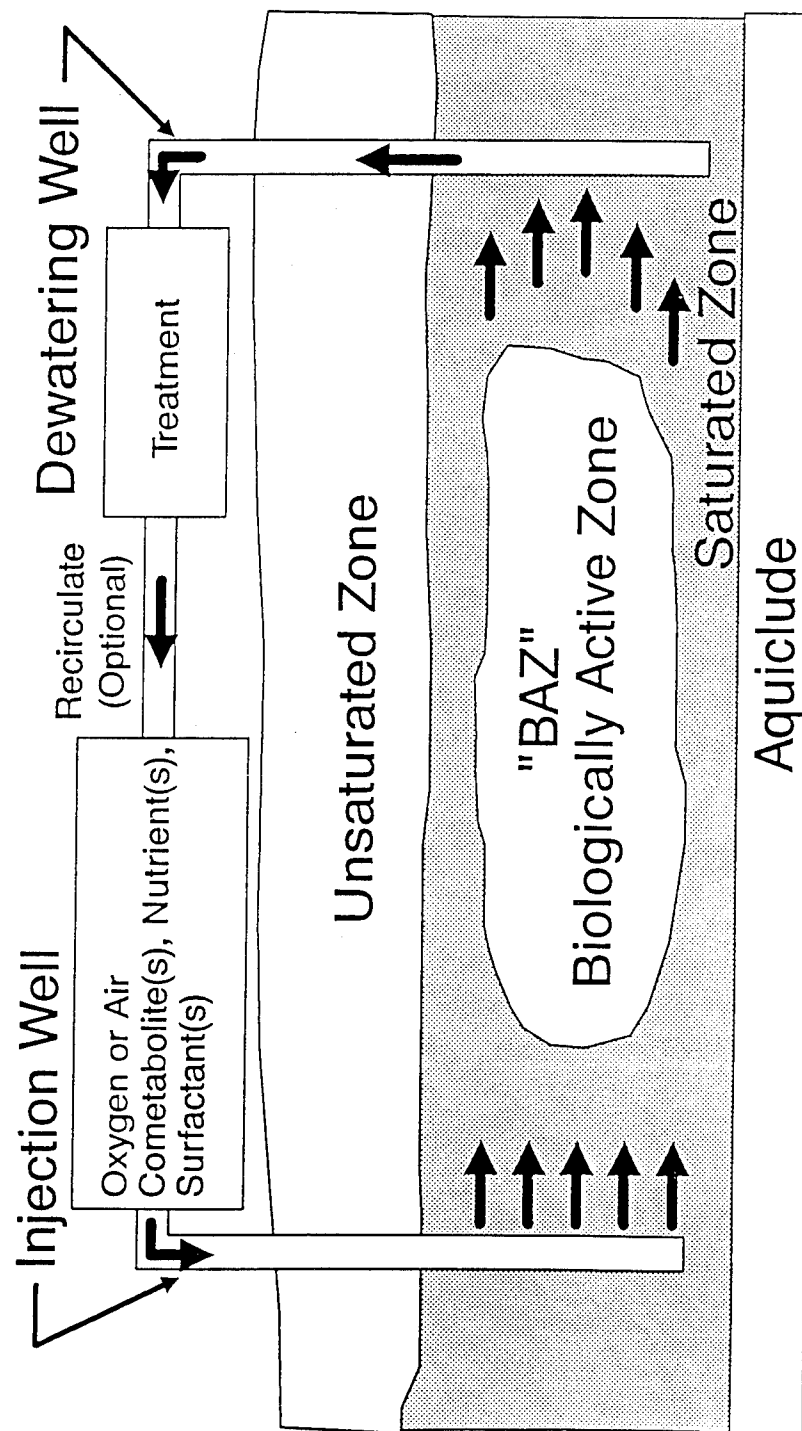


Figure 19. Saturated zone in situ biotreatment scenario

concentrations did not exceed 20 mg/L (11.7 grains/gal) and that many gram negative bacteria grew well on 100 mg TNT/L (58 grains TNT/gal) of solution. McCormick, Cornell, and Kaplan (1984) found no toxicity or mutagenicity due to RDX or HMX at concentrations as high as 200 mg/L (117 grains/gal) in anaerobic cultures.

TNT showed complicated elution characteristics due to heterogeneities in the distribution of TNT in the Crane 1.5 soil and due to the production of TNT transformation products. Heterogeneities in TNT contamination (crystalline versus sorbed) significantly affected elution behavior and have the potential to impact the feasibility of in situ remediation. Dissolution was the dominant interphase transfer process. Concentrations of 4A increased as TNT concentrations declined, although 4A increases were of smaller magnitude.

For cleanup of the contaminated zone, hydraulic residence time in the contaminated zone must be sufficient for biodegradation to degrade TNT to target levels. If pumping rates are too high, dissolution and transfer of explosives into flowing water may not be able to keep up with water flow. As a consequence, water from the withdrawal wells will indicate cleaner subsurface conditions than actually exist. TNT transformation products will probably appear in withdrawal wells during cleanup. A surface treatment system, as shown in Figure 19, is therefore needed, especially if recirculation is practiced. Subsurface heterogeneities can significantly affect the feasibility of the remediation scenario shown in Figure 19. Preferential flow causes some zones to receive very little flushing. Cleanup of explosives in these zone may be limited by diffusion into regions of mobile water.

Land farming

When explosive contamination resides in surface layers of unsaturated soil, land farming is an attractive bioremediation alternative. Land farming is implemented by surface tilling and application of aqueous solutions of nutrients, cometabolites, and, perhaps, surfactants (Figure 20). The BAZ is within the surface above a saturated zone, or groundwater. When explosive concentrations are high in the surface soil, particularly when free product abounds, application of water containing amendments will leach the solubilized explosive further into the BAZ. Microbial activity will have to be rapid enough to destroy the explosive before it migrates into groundwater. Therefore, knowledge of site hydrology and microbial effectiveness is important in land farming of surface soil highly contaminated with explosives. In the land-farming scenario, cleanup will be less affected by soil heterogeneities than in the scenario shown in Figure 19. When soil explosive levels are moderate to low and mobilization of explosives is driven by partitioning rather than solubilization of free product, maintaining a rate of microbial degradation rapid enough to prevent migration of free product to groundwater is less critical. Under this scenario, addition of surfactants may even be appropriate. However, increases in concentrations

Unsaturated Zone Biotreatment

"Landfarming"

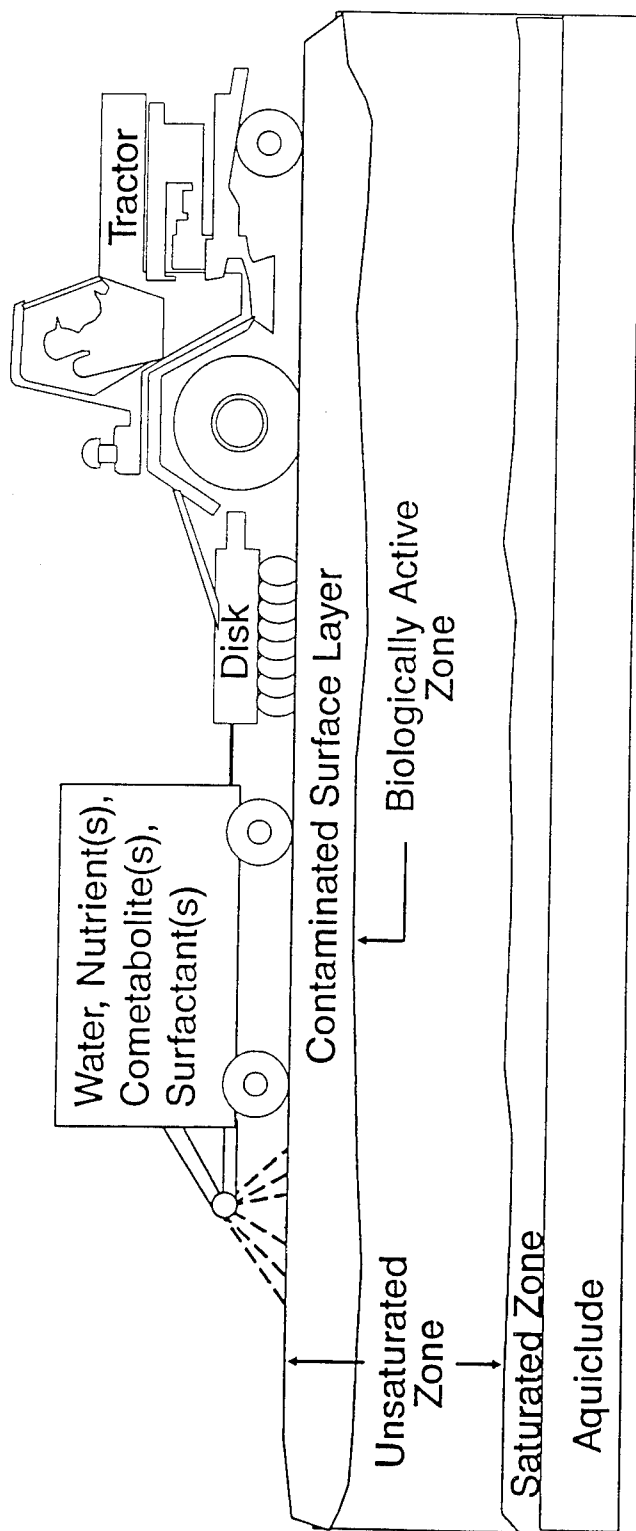


Figure 20. Scenario for land farming, or unsaturated zone biotreatment of near-surface contamination

of explosives in the solution phase were smaller when explosive concentrations were very low, e.g. in Crane 1.5 soil, than when explosive concentrations were high, e.g. in Hastings soil.

In situ biotreatment using injection and extraction wells

For in situ biotreatment of unsaturated soils, surface or injection wells are employed to introduce water containing additives. Subsequently, injected water moves by percolation or forced flow through the BAZ and is recovered via horizontal or vertical extraction wells (Figure 21). The amount of explosive in the mobile phase depends upon at least three factors; solution phase solubility of the explosive; characteristics of the soil, e.g. porosity and water holding capacity, and site hydrology, e.g. infiltration rates. For example, flooding of the soil will initially result in a highly heterogeneous flow field. During this phase, in situ bioremediation will be partially effective. The major constraint will not be sorption, but preferential flow. Eventually saturated conditions may extend from the surface to the leachate collection system. At this stage, preferential flow will be less a concern, but some zones will still receive less flow than others. In zones of little water movement, cleanup will be limited by diffusion to regions of mobile water.

Concentrations of TNT, RDX, and HMX in water percolating through the soil may exceed aqueous solubility due to association of the explosive with mobile particulate or colloidal materials. However, the rate of flow will make a significant contribution to the amount of contaminant mobilized. Bioavailability of the explosive will be high if soil concentrations are high, and especially if free product becomes dissolved. If soil concentrations of explosives are low, surfactants may be needed. Use of hot water may be considered when implementing this treatment scenario if surfactants are impractical. Hot water desorption is more effective in removing explosives from soil than water at ambient temperature, but not as effective as surfactants.

Unsaturated Zone Biotreatment

"Near-Surface Infiltration / Extraction"

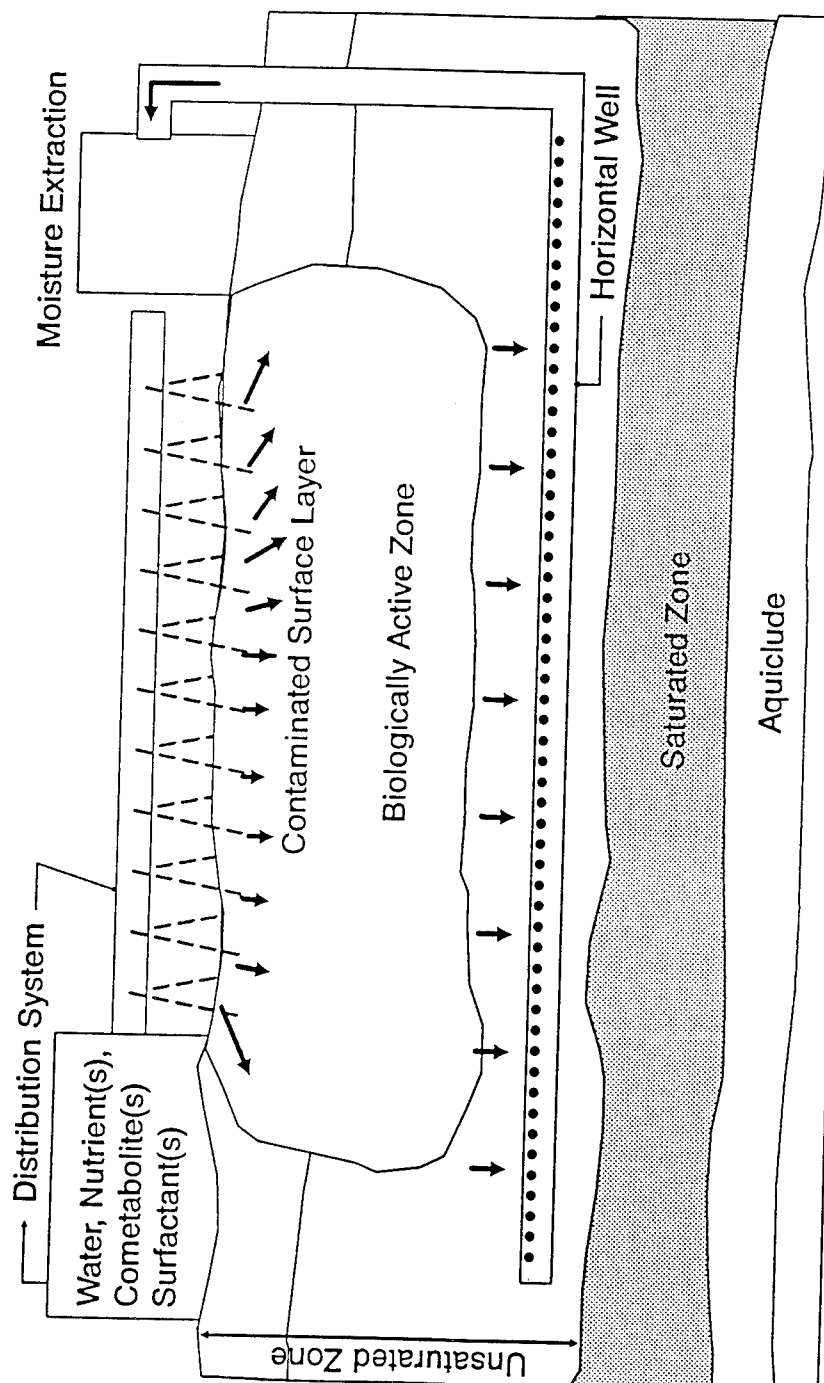


Figure 21. Unsaturated zone in situ biotreatment scenario using percolation and extraction wells

5 Conclusions

Concentration of explosive may be the most important factor to consider when selecting, evaluating, and designing an in situ bioremediation system for explosive-contaminated soils. Bioavailability of TNT, TNT transformation products, RDX, and HMX depends upon solubilization rather than processes such as desorption when explosive concentrations are high, especially when free product is present in the soil. When explosive concentrations are moderate to low, desorption processes control bioavailability.

Solution phase concentrations of TNT, RDX, and HMX in soils were controlled by the aqueous solubility of the respective explosives, except for TNT in Crane Sifter and Crane 1.5 soils. In Crane Sifter soil, which had a TNT concentration of 1,495 mg/kg (104 grains/lb), solution phase concentration was controlled by partitioning. The partition coefficient was 6.16, which is consistent with values reported in the literature (minimum 2.3 and maximum 11.0; Pennington and Patrick 1990). In Crane 1.5 soil, which had a TNT concentration of 25.8 mg/kg (1.80 grains/lb), leachable TNT was depleted below detection limits after a single aqueous challenge in batch tests. In the other two soils, Hastings and Weldon Springs, which were relatively high in explosives, solution phase concentrations of explosives remained near saturation in each challenge.

Partitioning resulted in nearly linear desorption isotherms for three TNT degradation products, 4A, 2A, and TNB. Partitioning coefficients for these products (6.06, 6.22, and 2.9, respectively) are within the range of the partitioning coefficient of TNT reported in the literature.

In the single soil tested with hot water, solution phase concentrations of TNT, RDX, and HMX were generally higher in kinetics tests with water at 55 °C than in water at 40 °C or at ambient temperature. However, TNT concentrations decreased to levels typical of ambient temperature by 5 days. Concentrations of 4A and TNB increased steadily over the same period suggesting transformation to these products due to elevated temperature. Solution phase concentrations of the explosives at 40 °C and at ambient temperature differed little. These results suggest that use of water at 55 °C will increase solution phase concentrations of the explosives, but will promote transformation of TNT to potentially harmful products.

The surfactants, Alfonic and Tween, increased solution phase concentrations of TNT, RDX, and HMX. Desorption isotherms for highly contaminated soils tended to be vertical indicating saturation of the surfactant/water phase. However, surfactant isotherms for 4A, 2A, and TNB resulted in partition coefficients ranging from 2.2 to 6.40. These values were slightly lower than partition coefficients with water alone. Solution phase concentrations with surfactants were generally 1.5 to 2 times greater than aqueous solubility or solution phase concentrations with water alone.

Surfactants may be unnecessary in highly contaminated soils if aqueous phase concentrations of explosives are already as high as microbial populations can tolerate. In soils exhibiting moderate concentrations of explosives where solution phase concentrations are determined by desorption, mobilization occurs readily, but may be enhanced by surfactants. When soil concentrations are low, surfactants may be most effective.

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High concentrations of explosives in the solution phase of soils are potentially toxic or inhibitory to the degrading microflora. Under land farming biotreatment, rates for injecting nutrients, surfactants, or hot water must be controlled so that contaminants are degraded fast enough in the biologically active zone to preclude leaching into groundwater. For injection/extraction well in situ bioremediation, flow rates must be optimized for maximum degradation rate, and extraction must be efficient if degradation is incomplete. Surfactants may be unnecessary in highly contaminated soils if solution phase concentrations of explosives are already as high as microbial populations can tolerate.

In soils exhibiting low concentrations of explosives where solution phase concentrations are determined by desorption, convection, and dispersion, mobilization and migration occur readily, but may be enhanced by addition of surfactants.